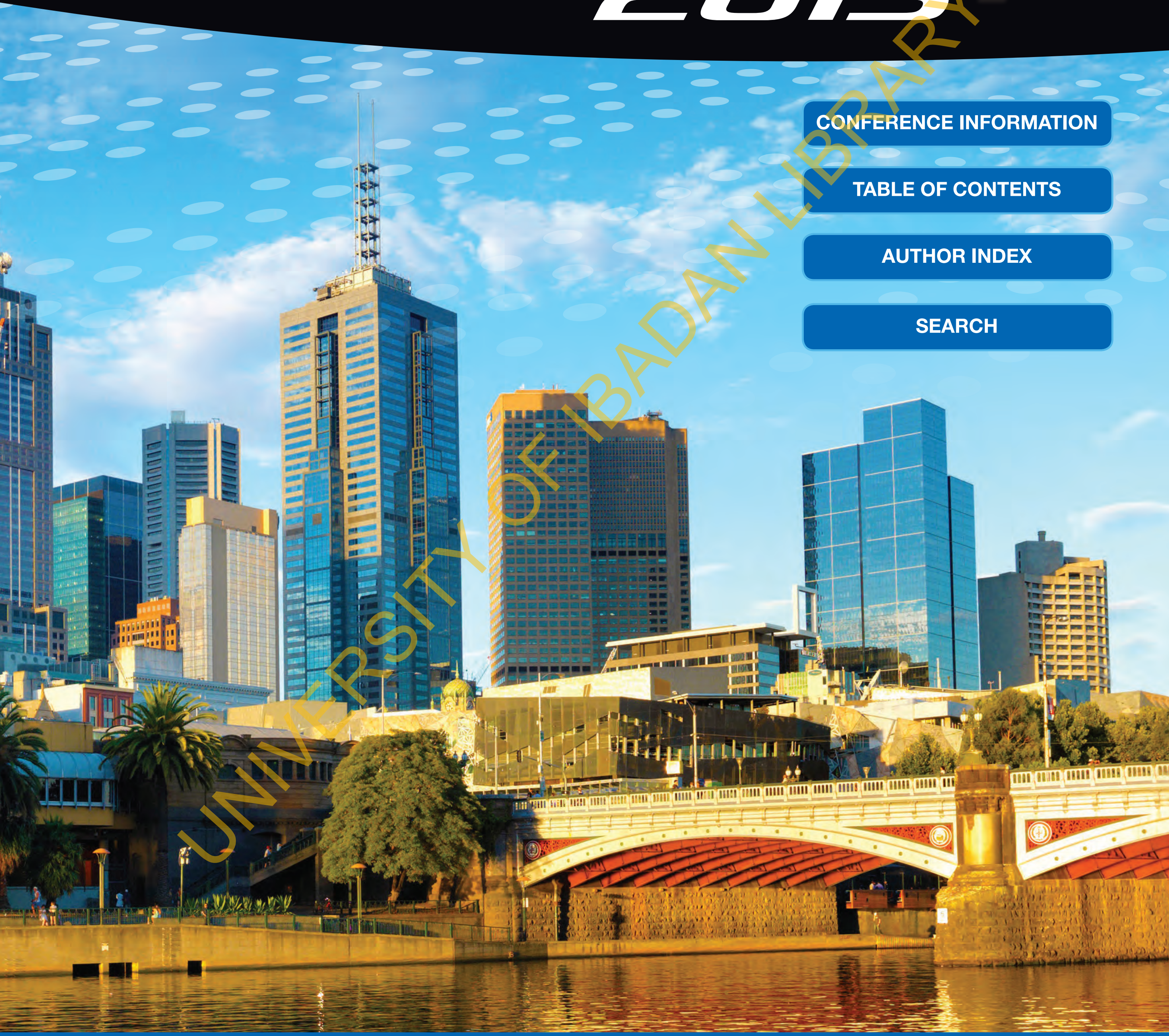
Proceedings

6th International Contaminated Site Remediation Conference

CleanUp 2015



CONFERENCE INFORMATION

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SEARCH

Crown Melbourne | 13 – 16 September 2015

Cooperative Research Centre for Contamination Assessment and Remediation of the Environment

September 2015

ISBN: 978-1-921431-47-0

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These proceedings should be cited as:

CRC CARE 2015, 6th International Contaminated Site Remediation Conference: Program and Proceedings, CleanUp 2015 Conference, Melbourne, Australia, 13–16 September 2015.

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WELCOME

On behalf of CRC CARE it is my pleasure to welcome you to the biennial CleanUp Conference.

This year, the organising committee has prepared a scientific and educational program that covers all aspects of contaminated site assessment, management and remediation. Particular attention has been paid to presenting you with different aspects and approaches from Australia and many other countries around the world. The sessions will cover both advances in research and industry best practice.

Whether you are an industry practitioner, a scientist, a regulator or a service provider, and regardless of whether you are new to the field or have been practicing for decades, we are certain that you will find something interesting at each time slot.

The organising committee is pleased to have once again secured the Crown Melbourne as the host venue for the event. The Crown Conference Centre – one of Australia's best-equipped purpose-built hotel convention facilities – is the ideal venue for the CleanUp Conference. Crown offers an environment that enables attendees to easily navigate the tightly paced program, engage with exhibitors, and share ideas and information.

Networking will be facilitated through lunches, receptions and other meals during program breaks. After the sessions conclude each evening, there will be poster sessions and networking drinks, and the Conference Gala Dinner will again be a highlight.

Bringing together over 700 delegates from all fields and related industries, the Conference presents an excellent opportunity to increase awareness of your organisation, demonstrate your involvement in the contamination assessment and remediation industry, promote your products and services, support your brand, and build your profile – before, during and after the event.

We encourage you to take advantage of this unique opportunity to promote yourself, your organisation and your clients to a large national and international audience, and to contribute to the success of this special event.

The Conference has again been very well supported by our sponsors and exhibitors, without whom CleanUp 2015 would not be possible.

Finally, we extend our thanks to the members of the organising committees who have generously given their time and expertise to ensure CleanUp 2015 meets the needs of the various industry sectors represented by the attending delegates.

We look forward to your participation at this year's Conference for what we are sure will be a professionally rewarding and enjoyable experience.

Professor Ravi Naidu
CEO and Managing Director, CRC CARE
Global Innovation Chair and Director,
Global Centre for Environmental Remediation, University of Newcastle

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The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) is a multi-partner Australian research organisation developing innovative technologies to assess, prevent and remediate the contamination of soil, water and air. World-class researchers at CRC CARE work with industry on global contamination issues, engaging with major end-users such as the mining and petroleum industries, environmental regulators, government organisations, small-to-medium sized enterprises and consultants.

CRC CARE's structured research program is complemented by a focus on educating and training postgraduates and industry professionals. In so doing, CRC CARE supports the growth of highly qualified and suitably trained researchers and decision-makers in the area of environmental risk assessment and remediation.

For more information, visit www.crccare.com

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Special thanks

The success of the CleanUp Conference series owes much to the commitment and vision of Andrew Beveridge, former CRC CARE Education and Training Program Leader. Andrew moved into a new role earlier this year, and we wish him luck for the future.

CONFERENCE OVERVIEW | SUNDAY - THURSDAY

		CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
Sunday,13 September 2015	8.30 – 10.00		*In-situ* bioremediation of chlorinated volatile organic compounds (VOCs) in groundwater	Integrated (LNAPL & DNAPL) site characterisation
	10.30 – 12.30			
	13.30 – 15.00		Data review basics	Use and measurement of mass flux and mass discharge
	15.30 – 17.00			
	17.00 – 17.30	Welcome reception - Level 2, Pre-function area		
	17.30 – 17.45	Official conference opening		
	17.45 – 18.45	Brian Robinson memorial lecture presented by Cheryl Batagol, Chairman, EPA Victoria		
Monday, 14 September 2015	8.30 – 10.10	Advances in bioremediation	International Committee on Contaminated Land (ICCL) - Introduction and update from ICCL meeting	Delineation and characterisation of NAPLs in the subsurface
	10.40 – 12.20	Advances in bioremediation	ICCL - State of the practice and policy - Brownfield regeneration	Delineation and characterisation of NAPLs in the subsurface
	13.20 – 15.00	Bioavailability/bioaccessibility of contaminants	ICCL - State of the practice and policy - Chlorinated solvent source zone remediation	Remediation and management of LNAPL in unsaturated and saturated zones
	15.30 – 17.00	Bioavailability/bioaccessibility of contaminants	ICCL - State of the practice and policy - Emerging contaminants	Remediation and management of DNAPL in unsaturated and saturated zones
	17.10 – 18.10	Drinks and poster session		
Tuesday, 15 September 2015	8.30 – 10.10	Advances in site characterisation	Defence Symposium INVITE ONLY	Risk based land management
	10.40 – 12.20	Advances in site characterisation		Case studies – contaminated site assessment, remediation and management
	13.20 – 15.00	Remediation panel		Case studies – contaminated site assessment, remediation and management
	15.30 – 17.00	globalCARE		Case studies – contaminated site assessment, remediation and management
	17.10 – 18.10	Poster session		
	19.00 – 19.30	Pre-dinner drinks - Level 2, Pre-function area		
	19.30 – 00.00	Gala dinner		
Wednesday, 16 September 2015	9.00 – 10.40	National remediation framework	Fractured rock sites	Field measurement and sampling
	11.10 – 12.50	Climate change and remediation	Fractured rock sites	Per-fluorinated compounds
	13.40 – 15.20	Climate change and remediation	International and Australian developments on remediation strategy decision making	Per-fluorinated compounds
	15.50 – 16.30	Closing plenary lecture: Professor Campbell Gemmell		
	16.30 – 17.00	Conference closing		
Thursday, 17 September 2015	8.20 – 17.30	Technical tour (a former service station, a thermal treatment facility, a leading instrumentation company, and a leading environmental laboratory)		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
	Sustainable remediation practice and benefits	Assessment of vapour intrusion
Health risk assessment of contaminated sites with multiple chemicals of concern	Design optimisation of environmental challenges	Assessment of vapour intrusion
Vapour intrusion	Metal(loid) assessment and remediation in soil and water	Impact of contaminants on human health
Vapour intrusion	On site remediation of contaminated land	Impact of contaminants on human health
Vapour intrusion	On site remediation of contaminated land	Advances in human health risk assessment
Contaminated land regulation and site audit process – clearing up the misunderstandings	Urban renewal	Advances in ecological risk assessment
	Drinks and poster session	
Data quality issues – different perspectives	Contaminants of emerging concern	Reducing uncertainty and risks in environmental investigations
Data quality issues – panel discussion	Contaminants of emerging concern	Ground gas
Advances in analytical measurement and methods	Development of assessment criteria	Reuse and rehabilitation of landfills
Role of measurement in supporting policy	Development of assessment criteria	Sustainable remediation
	Poster session Pre-dinner drinks - Level 2, Pre-function area Gala dinner	
Risk assessment of contaminants	Mine site remediation, revegetation and rehabilitation	Community consultation and contaminated site remediation
Nanotechnology for groundwater remediation	Mine site remediation, revegetation and rehabilitation	Advances in waste treatment and management
Early career researchers - Presentations	Advances in remediation technologies	Harnessing the value of waste

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
8:30 – 10:10	**MA1 Advances in bioremediation** **Chair: Ryan Wymore, Geosyntec Consultants**	**MB1 International Committee on Contaminated Land (ICCL): Introduction and update from ICCL meeting** **Chair: Arminda Ryan, NSW EPA**	**MC1 Delineation and characterisation of NAPLs in the subsurface** **Chair: David Major, Savron**
8:30	MA11 LESS IS MORE: AN EFFICIENT APPROACH TO IN SITU SOURCE TREATMENT USING ACCELERATED BIOREMEDIATION Eric Kern, Golder Associates Ltd	MB11 SUMMARY OF THE DISCUSSION AT THE ICCL MEETING Dominique Darmendrail, ICCL	MC11 VARIABILITY AND UNCERTAINTY ASSOCIATED WITH SAMPLING, ANALYSIS, AND RISK ASSESSMENT Naji Akladiss, Maine Department of Environmental Protection
8:50			
9:10	MA12 MOLECULAR BIOLOGICAL TOOLS TO IDENTIFY AND OVERCOME OBSTACLES TO SOURCE ZONE BIOREMEDIATION AT COMPLEX SITES Andrew Wollen, Microbial Insights	MB12 INDUSTRY PERSPECTIVE AND COMMENTARY Peter Nadebaum, GHD Pty Ltd	MC12 CHARACTERIZATION OF CONTAMINANT DISTRIBUTION TO MEET SITE-SPECIFIC REMEDIAL OBJECTIVES AT SPATIAL RESOLUTIONS APPROPRIATE TO SUBSURFACE CONDITIONS Gary Wealthall, Geosyntec Consultants
9:30	MA13 UNRAVELLING MICROBIAL BIOREMEDIATION OF ORGANOPHOSPHATES: A METAGENOMIC SYSTEMS-BIOLOGY APPROACH Thomas C. Jeffries, University of Western Sydney		MC13 HIGH RESOLUTION SITE CHARACTERIZATION: THE PATH TO SUCCESSFUL REMEDIES AND REDUCED COST Seth Pitkin, Stone Environmental
9:50	MA14 BIOREMEDIATION OF WEATHERED HYDROCARBON CONTAMINATED CLAY SEDIMENTS Kavitha Ramadass, University of South Australia	Discussion and questions	MC14 LNAPL TRANSMISSIVITY – WHEN TO USE IT AND A NOVEL WAY TO REFINE VOLUME ESTIMATES Travis Teoh, URS
10:10 – 10:40	**MORNING TEA**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
MD1 Vapour intrusion **Chair: Jonathan Medd, Golder Associates Pty Ltd** **Sponsor: Golder Associates Pty Ltd**	**ME1 Metal(loid) assessment and remediation in soil and water** **Chair: Mike Sieczkowski, JRW Bioremediation**	**MF1 Impact of contaminants on human health** **Chair: Julian Cribb, Julian Cribb & Associates**
MD11 RECENT DEVELOPMENTS FOR ASSESSMENT AND MANAGEMENT OF SOIL VAPOUR INTRUSION Ian Hers, Golder Associates Ltd	ME11 BIOPHYSICAL APPROACHES TO REMEDIATION OF HEAVY METAL(LOID) CONTAMINATED SOILS Nanthi Bolan, University of Newcastle / CRC CARE	MF11 POTENTIAL HEALTH IMPACTS OF TOXIC CHEMICALS IN FISH: THE CASE OF PEARL RIVER DELTA, SOUTH CHINA Ming Wong, Hong Kong Institute of Education
MD12 DESIGN, VERIFCATION AND DEVELOPMENT OF ACTIVE SOIL VAPOUR SAMPLING PORTS IN FRACTURED BASALT Daniel Hodges, Golder Associates Pty Ltd	ME12 APPLICATION OF A TOXICITY APPROACH TO EVALUATE FREE CYANIDE AND METAL CYANIDE COMPLEXES IN WATERS OF GOLD AND OTHER MINING Barry N. Noller, The University of Queensland	MF12 USING A LIFETIME PHYSIOLOGICALLY BASED PHARMACOKINETIC MODEL TO ESTABLISH ARSENIC DRINKING WATER GUIDANCE Zhaomin Dong, University of Newcastle
MD13 VAPOUR (TCE) INTRUSION AND THE RELOCATION OF PEOPLE FROM THEIR HOMES – THE CAUSE, THE RELOCATION, THE SCIENCE, THE OUTRAGE Danielle Marie Torresan, SA EPA	ME13 LONG-TERM IMMOBILIZATION OF As AND Pb CONTAMINATED SOIL USING WASTE OYSTER SHELLS Deok Hyun Moon, Chosun University	MF13 SOURCES, SPECIATION AND BIOAVAILABILITY OF HEAVY METAL(LOID)S IN COMPLEMENTARY MEDICINES Shankar Bolan, University of Newcastle
MD14 VAPOUR INTRUSION MITIGATION USING A DRAINAGE LAYER BELOW A LARGE COMMERCIAL FLOOR SLAB Rory Lane, BlueSphere Environmental	ME14 A TOWNWIDE STUDY INTO THE PRESENCE AND REMEDIATION OF LEAD TAILINGS – NORTHAMPTON, WESTERN AUSTRALIA Brad Dermody, Aurora Environmental	MF14 CONCENTRATION OF ARSENIC IN HOME GROWN VEGETABLES: HEALTH IMPLICATIONS Mohammad M. Rahman, University of South Australia
MORNING TEA		

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
10:40 – 12:20	**MA2 Advances in bioremediation Chair: Megharaj Mallavarapu, University of Newcastle / CRC CARE**	**MB2 ICCL: State of practice and policy – Brownfield regeneration Chair: Mitzi Bolton, EPA Victoria**	**MC2 Delineation and characterisation of NAPLs in the subsurface Chair: Charles Newell, GSI Environmental Inc**
10:40	MA21 IN SITU BIOREMEDIATION OF CHLORINATED SOLVENT SOURCES Hans Stroo, Stroo Consulting	MB21 STATE OF THE PRACTICE Paul Nathanail, University of Nottingham	MC21 REVIEW OF CHARACTERIZATION METHODS FOR NAPL SOURCE ZONE DELINEATION AND MASS ESTIMATION Grant Carey, Porewater Solutions
11:00			
11:20	MA22 FULL SCALE BIOREMEDIATION OF TRICHLOROETHENE Rachael Wall, Golder Associates Pty Ltd	MB22 STATE OF THE POLICY Joerg Frauenstein, UBA	MC22 INTEGRATED DNAPL SITE CHARACTERIZATION AND TOOLS SELECTION Ryan Wymore, Geosyntec Consultants
11:40	MA23 MODELLING NATURAL ATTENUATION: PLANNING RELIABILIY BY A LONG TERM PROGNOSIS? Martin Wegner, M&P GEONOVA GmbH		MC23 STATE OF THE ART IN DEVELOPING CONCEPTUAL SITE MODELS FOR DNAPL GROUNDWATER PLUMES Tamzen McBeth, CDM Smith
12:00	MA24 ENHANCEMENT OF BIODEGRADATION OF 1,1,1-TCA AND 1,1-DCA BY THE INJECTION OF EVO AND NUTRIENTS Gregory Carli, GHD	Discussion and questions	MC24 AQUIFER TESTING TO DETERMINE BEDROCK ANISOTROPY AND LNAPL FLOW PATHWAYS Rhonda Hastie, Kleinfelder
12:20 – 13:20	**LUNCH**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
MD2 Vapour intrusion **Chair: Kristi Hanson, Senversa**	**ME2 On-site remediation of contaminated land** **Chair: Annette Nolan, Enviropacific Services** **Sponsor: Enviropacific Services / ISOTEC**	**MF2 Impact of contaminants on human health** **Chair: Ming Wong, Hong Kong Institute of Education**
MD21 ATTENUATION FACTORS FOR CHLORINATED VOCS – LESSONS LEARNED THROUGH 15 YEARS OF VAPOR INTRUSION EVALUATION IN EXISTING BUILDINGS Helen Dawson, Geosyntec Consultants	ME21 RECENT ADVANCES IN IN-SITU REMEDIATION TECHNOLOGIES Will Caldicott, ISOTEC	MF21 CLEANSING A POISONED PLANET: CHEMICALS, SCIENCE COMMUNICATION AND GLOBAL PEOPLE POWER Julian Cribb, Julian Cribb & Associates
MD22 RESULTS FROM CONTINUOUS MONITORING OF CHLORINATED SOLVENT VAPORS: RAMIFICATIONS ON SOIL GAS, SUB-SLAB SOIL GAS AND INDOOR AIR SAMPLING Blayne Hartman, Hartman Environmental	ME22 IS THERE A FUTURE FOR ONSITE CONTAINMENT? Andrew Pruszinski, SA EPA	MF22 HUMAN GUT MICROBIOTA- ARE THESE KEY TO EFFECTIVE FUNCTIONING OF HUMAN METABOLISM Ravi Naidu, CRC CARE / University of Newcastle
MD23 PETROLEUM HYDROCARBONS – OXYGEN DEMAND MODEL AND DATABASE USED TO SUPPORT SCREENING DISTANCES Jackie Wright, EnRiskS	ME23 PERMEABLE REACTIVE BARRIER: AN EFFECTIVE IN-SITU REMEDIATION TECHNOLOGY Volker Birke, Ostfalia University of Applied Sciences	MF23 TOTAL ARSENIC LEVELS IN RICE FROM BANGLADESH AND HUMAN HEALTH IMPLICATIONS Shofiqul Islam, University of South Australia
MD24 VALIDATION OF TCE & PCE IN REMEDIAL EXCAVATIONS USING VAPOUR HEADSPACE IN VIAL SAMPLING Adrian Heggie, WSP|Parsons Brinckerhoff	ME24 COMBINING IN SITU CHEMICAL AND BIOLOGICAL OXIDATION FOR GROUNDWATER TREATMENT UNDER A PERFORMANCE BASED PROJECT DELIVERY PROGRAM Bruce Marvin, Geosyntec Consultants	MF24 HUMAN HEALTH IMPLICATIONS OF ARSENIC LEVELS IN A TROPICAL OPEN LAGOON Amii Usese, University of Lagos-Nigeria
	LUNCH	

MONDAY | 13:20 - 15:30

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
13:20 – 15:00	**MA3 Bioavailability / bioaccessibility of contaminants** **Chair: Mark Cave, British Geological Survey**	**MB3 ICCL: State of practice and policy – Chlorinated solvent source zone remediation** **Chair: Andrew Pruszinski, SA EPA**	**MC3 Remediation and management of LNAPL in unsaturated and saturated zones** **Chair: Tamzen McBeth, CDM Smith**
13:20	MA31 FROM BIOAVAILABILITY SCIENCE TO REGULATION OF ORGANIC CHEMICALS Kirk Semple, Lancaster University	MB31 STATE OF THE PRACTICE Hans Stroo, Stroo Consulting	MC31 CROSSING THE GAP: STAR TREATMENT OF HETEROGENOUS NAPL DISTRIBUTION David Major, Savron
13:40			MC32 MODELING LNAPL DEPLETION AT A FORMER XYLENE PROCESSING FACILITY (GERMANY) Grant Carey, Porewater Solutions
14:00	MA32 COMPARISON OF ORAL BIOAVAILABILITY OF BENZO[A]PYRENE IN SOILS USING RODENT AND SWINE MODEL Luchun Duan, University of Newcastle	MB32 STATE OF THE POLICY Jeff Heimerman, US Environmental Protection Agency	MC33 RECONSTRUCTING THE RELEASE AND LONGEVITY OF LNAPL PETROLEUM FUEL IN THE FACE OF LIMITED DATA USING A MULTI-COMPONENT, MULTI-PHASE MODELLING APPROACH Kaveh Sookhak Lari, University of South Australia, CSIRO
14:20	MA33 ENHANCING THE IMMOBILISATION OF LEAD BY PHOSPHATE USING A BIODEGRADABLE CHELATE Peter Sanderson, University of Newcastle		MC34 USE OF LNAPL TRANSMISSIVITY METRICS IN LNAPL REMEDIATION IN THE NEWER VOLCANICS FRACTURED BASALT – A CASE STUDY Keith Maxfield, AECOM Pty Ltd
14:40	MA34 INFLUENCE OF SOIL AGEING ON LEAD BIOAVAILABILITY MA Ayanka Wijayawardena, University of Newcastle	Discussion and questions	MC35 BIOSPARGE REMEDIATION OF LNAPL AND DISSOLVED PHASE PETROLEUM IMPACTS ADJACENT TO COMMERCIAL BUILDINGS Geof Ellis, Golder Associates Pty Ltd
15:00 – 15:30	**AFTERNOON TEA**		

MONDAY | 13:20 - 15:30

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
MD3 Vapour intrusion **Chair: Jackie Wright, EnRiskS**	**ME3 On-site remediation of contaminated land** **Chair: Jean Meaklim, Greencap** **Sponsor: Enviropacific Services / ISOTEC**	**MF3 Advances in human health risk assessment** **Chair: Brian Priestly, Monash University**
MD31 CHLORINATED VAPOUR INTRUSION – COST-EFFECTIVE SCREENING & MANAGEMENT USING INDOOR RADON Henry Schuver, US Environmental Protection Agency	ME31 IN SITU REMEDIATION OF PETROLEUM HYDROCARBONS Tom O'Callaghan, Enviropacific Services	MF31 A HISTORICAL DEVELOPMENT OF CHEMICAL MIXTURES HEALTH RISK ASSESSMENT METHODS AND APPLICATIONS Linda K. Teuschler, LK Teuschler & Associates
	ME32 IN SITU ENHANCED ANAEROBIC BIODEGRADATION OF BENZENE BY INJECTION OF A SULPHATE BASED SOLUTION Pedro Balbachevsky, URS Australia	
MD32 COMMUNITIES AND VAPOUR INTRUSION Lenny Siegel, Centre for Public Environmental Oversight (CPEO)	ME33 ENHANCING ISCO – STRATEGIES AND TOOLS Charles Grimison, Thiess Services Pty Ltd	MF32 DECISION MAKING AT CONTAMINATED SITES: ISSUES AND OPTIONS IN HUMAN HEALTH RISK ASSESSMENT Barrie C. Selcoe, CH2MHill
MD33 COMPLICATIONS OF AMBIENT SOURCES IN ASSESSING VAPOUR INTRUSION RISKS Kathleen Prohasky, ERM Australia	ME34 IN SITU CHEMICAL REDUCTION TREATMENT OF LEAD AND SILVER IN GROUNDWATER UPGRADIENT OF A DRINKING WATER SOURCE Gregory Carli, GHD	MF33 INNOVATIVE APPLICATIONS OF QUANTITATIVE HEALTH RISK ASSESSMENT Sophie Wood, ERM
MD34 VAPOUR INTRUSION – THE VALUE OF STRINGENT NOTIFICATION AND REPORTING REQUIREMENTS IN THE MANAGEMENT OF COMMUNITY RISKS Catherine Irwin, Golder Associates Pty Ltd	ME35 MANGANESE ACTIVATED PERSULFATE (MNAP) FOR THE TREATMENT OF A SOURCE ZONE: AN INNOVATIVE DUAL OXIDANT FORMULATION Bruce Marvin, Geosyntec Consultants	MF34 CADMIUM CHEMICAL FORM IN SOIL CONTAMINATION AND SIGNIFICANCE FOR HUMAN HEALTH RISK ASSESSMENT Barry N. Noller, The University of Queensland
AFTERNOON TEA		

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
15:30 – 17:10	**MA4 Bioavailability / bioaccessibility of contaminants** **Chair: Kirk Semple, Lancaster University**	**MB4 ICCL: State of practice and policy – Emerging contaminants** **Chair: Bruce Kennedy, CRC CARE**	**MC4 Remediation and management of DNAPL in unsaturated and saturated zones** **Chair: Naji Akladiss, Maine Department of Environmental Protection**
15:30	MA41 REACHING A CONSENSUS ON BIOAVAILABILITY MEASUREMENTS; A CASE STUDY OF Pb in DUTCH TOWN SOILS Mark Cave, British Geological Survey	MB41 STATE OF THE PRACTICE Charles Schaefer, CDM Smith	MC41 REMEDIATION IN THE YEAR 2025: HOW CLEANUP AT DNAPL SITES MIGHT EVOLVE Charles Newell, GSI Environmental Inc
15:50			
16:10	MA42 QUANTIFYING STATISTICAL RELATIONS BETWEEN COMMONLY USED IN VITRO MODELS FOR ESTIMATING LEAD BIOACCESSIBILITY Kaihong Yan, University of Newcastle	MB42 STATE OF THE POLICY C. Molenaar / E. Van Dyck	MC42 COMBINING IN SITU THERMAL WITH BIOREMEDIATION FOR DNAPL TREATMENT: PEFORMANCE AND DESIGN CONSIDERATIONS Tamzen McBeth, CDM Smith
16:30	MA43 ASSESMENT OF ARSENIC SPECIATION AND BIOACCESSIBILITY IN MINE-IMPACTED MATERIALS Cameron Ollson, University of South Australia		MC43 IN SITU SMOLDERING COMBUSTION (STAR) PRE-DESIGN EVALUATION (PDE) FOR L&DNAPL COAL TAR IN AN AQUIFER David Major, Savron
16:50	MA44 COPPER DECREASES ARSENIC SOLUBILITY, GROWTH AND UPTAKE AT TOXIC DOSE LEVELS (EC10 AND EC50) Mohammed Kader, University of Newcastle	Discussion and questions	MC44 A WEIGHT OF EVIDENCE APPROACH TO IN-SITU BIOREMEDIATION OF GROUNDWATER IN DNAPL SOURCE ZONES Jonathan Ho, AECOM
17:10 – 18:10	**DRINKS AND POSTER SESSION**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
MD4 Contaminated land regulation and site audit process – clearing up the misunderstandings **Chair: Ross McFarland, AECOM**	**ME4 Urban renewal** **Chair: Paul Vogel, WA EPA**	**MF4 Advances in ecological risk assessment** **Chair: Kenneth Kiefer, ERM**
MD41 CONTAMINATED LAND REMEDIATION – DETERMINING ENDPOINTS Erwin Benker, NSW EPA	ME41 URBAN RENEWAL: PREPARING FOR A JOURNEY NOT PACKING FOR A DESTINATION Paul Nathanail, University of Nottingham	MF41 CHALLENGES WITH SOILS CONTAMINATED BY MIXED CONTAMINANTS: BIOAVAILABILITY, BIOREMEDIATION AND ECOTOXICITY CONSIDERATIONS Megharaj Mallavarapu, University of Newcastle / CRC CARE
MD42 A REGULATOR'S PERSPECTIVE ON THE CLEAN UP OF GROUNDWATER AND EPA VICTORIA'S REFORM PROCESS Anne Northway, EPA Victoria		
MD43 PRACTICAL IMPLICATIONS FOR REMEDIATION WASTE MANAGEMENT RESULTING FROM NEW NSW REGULATIONS AND DRAFT SITE AUDITOR GUIDELINES Sophie Wood, ERM	ME42 MODELS AND LESSONS FOR DEVELOPING A CONTAMINATED SITE PROGRAM: AN INTERNATIONAL REVIEW Walter W. Kovalick, 8th Avenue Consulting	MF42 ASSESSMENT OF GROUNDWATER – SURFACE WATER INTERACTION IN A FRACTURED BASALT AQUIFER SYSTEM TO SUPPORT ECOLOGICAL RISK ASSESSMENT Frederic Cosme, Golder Associates Pty Ltd
MD44 ENVIRONMENTAL AUDIT REFORM: IS IT JUST ABOUT THE RED TAPE? Joanna Missen, EPA Victoria	ME43 FISHERMANS BEND URBAN RENEWAL AREA: PROACTIVE GROUNDWATER BACKGROUND STUDIES German Ferrando-Miguel, EPA Victoria	MF43 LINES OF EVIDENCE USED IN ECOLOGICAL RISK ASSESSMENT OF CONTAMINATED GROUNDWATER Kirsten Broadgate, Golder Associates Pty Ltd
MD45 NSW vs WA: WHO IS BETTER AT REGULATING CONTAMINATED LAND? Sarah Mansfield, Henry Davis York	ME44 COMMUNITY CONSULTATION IN AN URBAN RENEWAL PROJECT AND COMPETING OBJECTIVES Vanessa Bryant, Ramboll Environ Australia Pty Ltd	MF44 ASSESSMENT OF WEATHERED HYDROCARBON RESIDUAL TOXICITY USING ENDEMIC AUSTRALIAN FLORA AND FAUNA Muhammad Atikul Islam Khan, University of South Australia
	DRINKS AND POSTER SESSION	

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
8:30 – 10:10	**TA1 Advances in site characterisation** **Chair: Gary Wealthall, Geosyntec Consultants**	**TB1 Defence Symposium**	**TC1 Risk based land management** **Chair: Prashant Srivastava, CRC CARE**
8:30	TA11 USING IN SITU REMEDIATION (ISR-MT3DMS) MODEL TO ESTIMATE BACK-DIFFUSION TIMEFRAME FOR THIN SILTS AND CLAYS Grant R. Carey, Porewater Solutions	DEFENCE SYMPOSIUM - INVITATION ONLY	TC11 RISK BASED LAND MANAGEMENT: WHAT IT IS; WHAT IT IS NOT Paul Nathanail, University of Nottingham
8:50	TA12 FORMER CLANDESTINE DRUG LABORATORIES – HOW CONTAMINATED ARE THEY? Jackie Wright, EnRiskS		
9:10	TA13 WHEN CONCEPTUAL SITE MODELS ARE WRONG – A CASE STUDY Penelope R. Woodberry, Golder Associates Pty Ltd		TC12 SUSTAINABLE DEVELOPMENT OF BROWNFIELDS Surampalli Rao, Global Institute for Energy, Environment and Sustainability
9:30	TA14 ASSESSING BACKGROUND CONCENTARTIONS OF INORGANIC CONTAMINANTS IN THE BRIGHTON GROUP AQUIFER, SOUTHEAST MELBOURNE Megan Gaffney, ACLCA Victoria		TC13 INNOVATIVE LNAPL CONCEPTUAL SITE MODEL DEVELOPMENT TOOLS IN SUPPORT OF MORE SUSTAINABLE RISK-BASED LNAPL SITE MANAGEMENT Matthew Rousseau, GHD Pty Ltd
9:50	TA15 PERFORMANCE TESTING OF SUPER OXYGENATED WATER GENERATION AND DELIVERY METHODS Jessica K. Ewers, Golder Associates Pty Ltd		TC14 REMEDIATION END POINT: RISK BASED OR PUBLIC PERCEPTION? CASE STUDY OF THE REMEDIATION OF A PETROLEUM HYDROCARBON PLUME IN PERTH, WESTERN AUSTRALIA Penelope L. King, Environmental Strategies
10:10 – 10:40	**MORNING TEA**		

TUESDAY | 8:30 - 10:40

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
TD1 Data quality issues – different perspectives **Chair: Cheryl Lim, National Measurement Institute / CRC CARE**	**TE1 Contaminants of emerging concern** **Chair: Daniel Slee, National Measurement Institute** **Sponsor: CH2M**	**TF1 Reducing uncertainty and risks in environmental investigations** **Chair: Therese Manning, EnRiskS**
INTRODUCTION REGULATOR'S PERSPECTIVE Erwin Benker, NSW EPA LABORATORY'S PERSPECTIVE David Springer, Envirolab CONSULTANT'S / AUDIOR'S PERSPECTIVE Phil Sinclair, Coffey LANDOWNER'S PERSPECTIVE Craig Barnes, Airservices CLOSING REMARKS	TE31 EMERGING ENVIRONMENTAL CONTAMINANTS AND CURRENT ISSUES Susan Richardson, University of South Carolina	TF11 REDUCING UNCERTAINITY DURING REMEDIAL DESIGN – A CASE STUDY Charles Grimison, Thiess Services Pty Ltd
		TF12 USING MASS BALANCE IN RISK ASSESSMENT Kenneth Kiefer, ERM
	TE32 NATURE, ENVIRONMENTAL FATE, AND POTENTIAL HUMAN AND AQUATIC TOXICITY OF POLAR METABOLITE MIXTURES IN GROUNDWATER AT BIODEGRADING FUEL RELEASE SITES ***PRE-RECORDED VIDEO*** Dawn Zemo, Zemo & Associates Inc	TF13 FAST TRACKED: THE ENVIRONMENTAL RISKS AND CHALLENGES OF GRADE SEPARATION PROJECTS Alessandro Sica, Golder Associates Pty Ltd
	TE33 PROVIDING THE INFRASTRUCTURE NEEDED TO IMPROVE THE QUALITY OF PBDE MEASUREMENTS IN AUSTRALIA Gavin Stevenson, National Measurement Institute	TF14 OCCUPATIONAL HYGIENE IN THE REMEDIATION INDUSTRY: A REVIEW OF RISK IN RECENT CASE STUDIES DURING GASWORKS REMEDIATION Kate Cole, Thiess Services
	TE34 DETERMINING LEVELS OF PBDES ON CONTAMINATED SITES AND ASSESSING THE IMPLICATIONS FOR SITE REMEDIATION IN AUSTRALIA Thomas McGrath, RMIT University	TF15 ASSESSING CONTAMINATED SITES DATA – TRADING ACCURACY FOR KNOWLEDGE Peter Beck, GHD Pty Ltd

MORNING TEA

TUESDAY | 10:40 - 13:20

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
10:40 – 12:20	**TA2 Advances in site characterisation** **Chair: Tamie Weaver, ERM**	**TB2 Defence Symposium**	**TC2 Case studies – contaminated site assessment, remediation and management** **Chair: Raghava Dasika, URS**
10:40	TA21 RECENT DEVELOPMENTS IN IDENTIFICATION OF UNKNOWN CONTAMINATION SOURCES AND MONITORING NETWORK DESIGN FOR CONTAMINATED GROUNDWATER SYSTEMS Bithin Datta, James Cook University	DEFENCE SYMPOSIUM – INVITATION ONLY	TC21 FIRST APPLICATION OF THE SUPER OXYGENATED WATER (SOW) TECHNOLOGY IN AUSTRALIA: CASE STUDY FOR SANDY SOILS Paolo Arcidiacono, Golder Associates Pty Ltd
11:00			TC22 POINT COOK THERMAL DESORPTION REMEDIATION PROJECT Will Magnus, Enviropacific Services
11:20	TA22 ANALYTE ION DETECTION METHOD AND DEVICE (probeCARE) Liang Wang, University of Newcastle		TC23 MACDONALDTOWN GASWORKS – AN MGP CASE STUDY Adam Fletcher, Thiess Services Daniel Wedgwood, Sydney Trains
11:40	TA23 EVALUATION OF STATISTICAL AND GEOCHEMICAL METHODS FOR DISTINGUISHING SOIL CONTAMINATION FROM BACKGROUND CONCENTRATIONS Hannah Mikkonen, RMIT University		TC24 COST EFFECTIVE CUTEP REMEDIATION AND METRICS UTILISING LNAPL TRANSMISSIVITY David Jackson, Environmental Strategies
12:00	TA24 THE USE OF CONTAMINANT MASS FLUX AND MASS DISCHARGE TO SUPPORT GROUNDWATER REMEDIATION AT A HISTORICAL GASWORKS, BARANGAROO, SYDNEY AUSTRALIA Graham Hawkes, AECOM		TC25 DEVELMENT OF TECHNOLOGY FOR REMOVAL OF URANIUM FROM CONTAMINATED SOIL USING INDOOR ELECTROKINETIC DECONTAMINATION EQUIPMENT Gye-Nam Kim, Korea Atomic Energy Research Institute
12:20 – 13:20	**LUNCH**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
TD2 Data quality issues – panel discussion **Chair: Neil Shepherd, NATA**	**TE2 Contaminants of emerging concern** **Chair: Joytishna Jit, University of South Australia / CRC CARE** **Sponsor: CH2M**	**TF2 Ground gas** **Chair: David Adams, Environmental Strategies** **Sponsor: Environmental Strategies**
Panel discussion	TE21 EMERGING CONTAMINANTS UPDATE, WITH A FOCUS ON PER- AND POLYFLUOROALKYL SUBSTANCES AND 1,4-DIOXANE William H. Diguiseppi, CH2M	TF21 GROUND GAS RISK MANAGEMENT – LESSONS LEARNT FROM AN AUDITOR'S PERSPECTIVE Tim Chambers, Environmental Strategies
	TE22 KEY ISSUES REGARDING THE FATE AND TRANSPORT OF EMERGING CONTAMINANTS Charles Schaefer, CDM Smith	TF22 INSTALLATION AND PILOT TRIAL OF SOIL VAPOUR EXTRACTION (SVE) FROM A HORIZONTAL WELL IN THE NEWER VOLCANICS BASALT BENEATH AND OPERATING PLANT BUILDING Patrick Clarke, Senversa Pty Ltd
	TE23 RISK-BASED MANAGEMENT AND REMEDIATION FOR BENZO(A)PYRENE Peter Nadebaum, GHD Pty Ltd	TF23 ASSESSING THE HYDROCARBON NATURAL SOURCE ZONE DEPLETION RATE OF NON-AQUEOUS PHASE HYDROCARBONS BY MEASURING SOIL GAS FLUX Danny McDonald, Cardno
	TE24 INVESTIGATION OF EMERGING CONTAMINANTS IN ENVIRONMENTAL WATERS Yvonne Yin, National Measurement Institute	TF24 THE USE OF PASSIVE SOIL GAS (PSG) SURVEYS TO IMPROVE THE USABILITY OF INFORMATION GATHERED DURING PRELIMINARY SITE INVESTIGATIONS AT PETROLEUM CONTAMINATED SITES Paul R.D. Wright, WrightKunsult Environmental Solutions
LUNCH		

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
13:20 – 15:00	**TA3 Remediation panel** **Chair: David Reynolds, Geosyntec Consultants / David Thomas, Chevron** **Sponsor: Geosyntec Consultants**	**TB3 Defence Symposium**	**TC3 Case studies – contaminated site assessment, remediation and management** **Chair: Louise Cartwright, Enviropacific Services**
13:20	The panel will consist of representatives from industry, consulting, research, and regulatory bodies. This is an interactive session discussing various environmental topics of interest. The session will include brief presentations by panel members followed by a moderated discussion and debate. Audience participation technology (keypad clickers) will be available for attendees.	DEFENCE SYMPOSIUM – INVITATION ONLY	TC31 LONG-TERM BIOEMEDIATION AND MANAGEMENT FOR A CO-MINGLED CHLORINATED SOLVENT AND 1,4-DIOXANE SOURCE AREA AND PLUME Ryan Wymore, Geosyntec Consultants
13:40			TC32 TOWARDS SUSTAINABLE REMEDIATION IN THE 21ST CENTURY: DEFINED MECHANOCHEMICAL REDUCTIVE DEHALOGENATION AT ROOM TEMPERATURE IN A BALL MILL Volker Birke, Ostfalia University of Applied Sciences
14:00			TC33 QUANTIFYING THE MASS OF PETROLEUM HYDROCARBON CONTAMINANTS DEGRADED BY MICROBIAL PROCESSES AT AN ACTIVE REMEDIATION SITE Stephen Cambridge, Coffey
14:20			TC34 BETTER MANAGEMENT OF REMEDIATION PROCESS UNCERTAINTY Christian M Borovac, Golder Associates Pty Ltd
14:40			TC35 ADVANCES IN FIELD SAMPLING: NO-FLOW VERSUS LOW-FLOW Claire Howell, WSP Parsons Brinckerhoff
15:00 – 15:30	**AFTERNOON TEA**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
TD3 Advances in analytical measurement and methods **Chair: Scott Fraser, PerkinElmer** **Sponsor: PerkinElmer**	**TE3 Development of assessment criteria** **Chair: Jack Dempsey, EnRiskS**	**TF3 Reuse and rehabilitation of landfills** **Chair: Tim Marshall, Coffey**
TD31 SINGLE PARTICLE ICP-MS (SP-ICP-MS) FOR THE DETECTION OF METAL-BASED NANOPARTICLES IN ENVIRONMENTAL MATRICES Chady Stephan, PerkinElmer	TE31 APPLICATION OF SITE SPECIFIC ADSORPTION ISOTHERMS FOR DERIVING SOIL REMEDIATION GOALS PROTECTIVE OF GROUNDWATER – TOOWOOMBA GASWORKS CASE STUDY Barry Mann, GHD Pty Ltd	TF31 AN INTEGRATED INVESTIGATION APPROACH FOR CHARACTERISATION OF A LANDFILL LEACHATE PLUME Lange B. Jorstad, Geosyntec Consultants
	TE32 REVIEW OF ECOLOGICAL INVESTIGATION LEVELS FOR TOTAL PETROLEUM HYDROCARBONS Therese Manning, EnRiskS	TF32 STRATEGIES IN MANAGING RISK OF LANDFILL GAS MIGRATION Aidan Marsh, Pacific Environment
TD32 DETERMINATION OF TOTAL RECOVERABLE HYDROCARBONS (TRH) IN SOIL USING SOXHLET EXTRACTION AND GC-FID Gabriela Saveluc, National Measurement Institute	TE33 RISK-BASED SCREENING CRITERIA FOR PCR USE OF WATER: IS 10 TIMES THE DRINKING WATER GUIDELINE PROTECTIVE? Kristi L. Hanson, Senversa Pty Ltd	TF33 AN AUSTRALIA-WIDE ASSESSMENT OF PERSISTENT, BIOACCUMULATIVE AND TOXIC CHEMICALS (PBTS) IN LANDFILL LEACHATES Christie Gallen, University of Queensland
TD33 TOTAL RECOVERABLE HYDROCARBONS IN WATERS: A CHEMIST'S PERSPECTIVE ON THE ANALYSIS OF SEMIVOLATILE PETROLEUM HYDROCARBONS Marc Centner, ALS Environmental	TE34 A CASE FOR HIL E – HEALTH INVESTIGATION LEVELS FOR INDIGENOUS AUSTRALIAN COMMUNITIES LIVING A TRADITIONAL LIFESTYLE Emmylou F. Cooke, Thiess Services	TF34 EFFECTIVE RESIDENTIAL REDEVELOPMENT OF A METHANEPRODUCING FORMER LANDFILL SITE, MELBOURNE, VICTORIA Warren Pump, ERM
TD34 DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SPIKED AND AGED SOIL USING MODIFIED QuEChERS AND GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY Vincent Lal, University of Queensland	TE35 DEVELOPING GROUNDWATER TIER 1 SCREENING CRITERIA FOR CHRONIC AND ACUTE VAPOUR RISKS FOR CHLORINATED HYDROCARBONS Kathleen Prohasky, ERM Australia	TF35 LNAPL EXTRACTION PRACTICABILITY ASSESSMENT – FORMER HAZARDOUS WASTE LANDFILL, TULLAMARINE, VIC, AUSTRALIA Alex Schiavoni, EHS Support

AFTERNOON TEA

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
15:30 – 17:10	**TA4 globalCARE** **Chair: Ravi Naidu, CRC CARE** **Sponsor: CRC CARE**	**TB4 Defence Symposium**	**TC4 Case studies – contaminated site assessment, remediation and management** **Chair: Neil Proposch, Aurecon**
15:30			TC41 RISK ASSESSMENT FOR LARGE FACILITIES OR PROGRAMS Barrie Selcoe, CH2MHill
15:50			TC42 DREDGING SYDNEY HARBOUR, ENVIRONMENTAL CONSIDERATIONS Ryan Well, Environmental Strategies
16:10	Launch of the Global Contamination and Remediation Enterprise (globalCARE). An overview will be presented by Ravi Naidu and Walter Kovalick.	DEFENCE SYMPOSIUM – INVITATION ONLY	TC43 COMPARISON OF IN-SITU SELF-SUSTAINING SMOULDERING COMBUSTION AND SEPR/S-ISCO METHODS FOR THE REMEDIATION OF COAL TAR DNAPL, BACCHUS MARSH, VICTORIA Matt Edwards, BlueSphere Environmental
16:30			TC44 DIRECT INJECTION OF EMULSIFIED VEGETABLE OIL FOR CHLORINATED SOLVENTS REMEDIATION Jessica Byrne, AECOM
16:50			TC45 MULWALA EXPLOSIVES AND CHEMICAL MANUFACTURING FACILITY – AN INTEGRATED APPROACH TO GROUNDWATER MANAGEMENT Melissa Saunders, AECOM Pty Ltd
17:10 – 18:10	**DRINKS AND POSTER SESSION**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
TD4 Role of measurement in supporting policy **Chair: Paul Vogel, WA EPA**	**TE4 Development of assessment criteria** **Chair: Bruce Kennedy, CRC CARE**	**TF4 Sustainable remediation** **Chair: John Hunt, EIC Activities** **Sponsor: SuRF ANZ**
TD41 THE ROLE OF MEASUREMENT AND QUALITY ASSURANCE IN SUPPORTING ENVIRONMENTAL POLICY AND REGULATION FOR CONTAMINATION MANAGEMENT Cheryl Lim, National Measurement Institute / CRC CARE	TE41 NATIONAL GUIDANCE FOR EMERGING CONTAMINANTS AT CRC CARE Joytishna Jit, CRC CARE	TF41 THREE REASONS TO CONSIDER SUSTAINABLE REMEDIATION (SR) A GLOBAL PERSPECTIVE AND A MUTUAL INTEREST Hans Slenders, Arcadis
TD42 PRODUCING TELEPHONE NUMBERS RATHER THAN REAL DATA FOR OUR MULTI-MILLION DOLLAR DECISION MAKING. A REVIEW OF DECISION CERTAINTY IN CONTAMINATED LAND ASSESSMENT AND REMEDIATION Ross McFarland, AECOM Australia Pty Ltd	TE42 RISK BASED ASSESSMENT, MANAGEMENT AND REMEDIATION OF PFOS AND PFOA Peter Nadebaum, GHD Pty Ltd	
TD43 CHALLENGES IN THE MEASUREMENT OF PFOS IN ENVIRONMENTAL SAMPLES: ARE THE NUMBERS MEANINGFUL TO ENVIRONMENTAL TOXICOLOGISTS AND REGULATORS Marc Centner, ALS	TE43 RISK-BASED METHODS TO DERIVE AQUATIC ECOSYSTEM GUIDELINES Kirsten Broadgate, Golder Associates Pty Ltd	TF42 SUSTAINABLE PRACTICE APPLICATION TO AUSTRALIAN AND REGIONAL REMEDIATION PROJECTS Garry J Smith, Geosyntec Consultants
TD44 THE VALUE OF THE RIGHT RATHER THAN ACCURATE MEASUREMENT IN CHARACTERISING CONTAMINATED SITES Peter Beck, GHD	TE44 ADVANCES IN THE DETERMINATION OF A HUMAN HEALTH SCREENING CRITERIA FOR 6:2 FLUOROTELOMER SULFONATE Ruth Jarman, EnRiskS	TF43 REDUCING CONTAMINATED MATERIAL DISPOSAL VOLUMES – A SUSTAINABLE AND COST EFFECTIVE REMEDIATION APPROACH Yvonne Binai, GHD Pty Ltd
TD45 ENVIRONMENTAL MEASUREMENTS AS THE BASIS OF POLICY CHANGE – A CASE OF THE TAIL WAGGING THE DOG? Dave Reynolds, Geosyntec	TE45 DERIVING CRITERIA FOR DIOXINS AND FURANS Olivia Henderson, WSP|Parsons Brinckerhoff	TF44 REMEDIATION IN THE CONTEXT OF GLOBAL SUSTAINABILITY Kevin Simpson, EHS Support
	DRINKS AND POSTER SESSION	

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
9:00 – 10:40	**WA1 National remediation framework** **Chair: Kerry Scott, CRC CARE** **Sponsor: CRC CARE**	**WB1 Fractured rock sites** **Chair: Raghava Dasika, URS** **Sponsor: Geosyntec**	**WC1 Field measurement and sampling** **Chair: Bill Stavropoulos, SGS Leeder Consulting** **Sponsor: SGS Leeder Consulting**
9:00	WA11 THE NATIONAL REMEDIATION FRAMEWORK – TOWARDS HARMONISATION Bruce Kennedy, CRC CARE	WB11 SUBSURFACE CHARACTERISATION, MODELLING, MONITORING, AND REMEDIATION OF FRACTURED ROCKS Dave Reynolds, Geosyntec	WC11 PERMEATION PASSIVE SAMPLING IN ENVIRONMENTAL ANALYSIS Tadeusz Gorecki, University of Waterloo
9:20			
9:40	WA12 OVERVIEW OF THE GUIDELINES FOR PERFORMING COST BENEFIT AND SUSTAINABILITY ANALYSIS OF REMEDIAL ALTERNATIVES Susan Barnes, CH2M	WB12 GEOLOGICAL INVESTIGATION USING MULTIPLE LINES OF EVIDENCE TO DETERMINE LNAPL PRESENCE IN BEDROCK Rhonda Hastie, Kleinfelder	WC12 A NEW METHOD FOR PERIMETER SAMPLING OF VOCs – "U.S. EPA METHOD 325: VOLATILE ORGANIC COMPOUNDS FROM FUGITIVE AND AREA SOURCES" Kristian Hansen, SGS
10:00	WA13 SUMMARY OF FOUR NATIONAL REMEDIATION FRAMEWORK GUIDELINES Luke Clements, CH2M	WB13 DEVELOPING CONCEPTUAL SITE MODELS FOR THE INVESTIGATION AND REMEDIATION OF FRACTURED ROCKS Gary Wealthall, Geosyntec Consultants Inc	WC13 RAPID ASSESSMENT OF A LARGE INDUSTRIAL MANUFACTURING SITE USING WMS-LU PASSIVE SOIL VAPOUR SAMPLERS Matthew B. Collyer, Edge Group Pty Ltd
10:20	WA14 IDENTIFYING AND ASSESSING CONTAMINATED SITE REMEDIATION OPTIONS Peter Nadebaum, GHD Pty Ltd	WB14 FRACTURED NEWER VOLCANIC BASALT – UNDERSTANDING KEY PROPERTIES THAT INFLUENCE REMEDIATION EFFICACY Jonathan Medd, Golder Associates Pty Ltd	WC14 A COMPARISON OF PASSIVE SAMPLING AND LOW-FLOW OR BAILED SAMPLING RESULTS ACROSS A RANGE OF AUSTRALIAN HYDROGEOLOGICAL SETTINGS Kenneth Kiefer, ERM
10:40 – 11:10	**MORNING TEA**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
WD1 Risk assessment of contaminants **Chair: Sophie Wood, ERM**	**WE1 Mine site remediation, revegetation and rehabilitation** **Chair: Nanthi Bolan, University of Newcastle / CRC CARE**	**WF1 Community consultation and contaminated site remediation** **Chair: Rebecca Hughes, SA EPA**
WD11 COMBINED GENOTOXIC EFFECT OF ARSENIC, CADMIUM, CHROMIUM AND FOUR POLYAROMATIC HYDROCARBONS Jack C. Ng, University of Queensland	WE11 CHALLENGES FOR NATIVE FOREST ESTABLISHMENT ON SURFACE MINES IN A TIME OF CLIMATE CHANGE Chris Barton, University of Kentucky	WF11 SOCIETAL PERCEPTIONS AND ACCEPTABILITY OF REMEDIATION TECHNOLOGIES Jason Prior, University of Technology Sydney
WD12 EVALUATING CHROMIUM SPECIATION IN GROUNDWATER TO GUIDE RISK ASSESSMENT AND REMEDIATION DECISIONS Tamie Weaver, ERM	WE12 WEB BASED GUIDANCE FOR MINE WASTE REMEDIATION Michael R. Sieczkowski, JRW Bioremediation	WF12 REAL RISK VERSUS PERCEIVED RISKIN THE REMEDIATION INDUSTRY Kristy Thornton, Thiess Services
WD13 RAPID RISK ASSESSMENT TO ADDRESS PUBLIC HEALTH CONCERNS REGARDING POTENTIAL EXPOSURE TO ANTIMONY Madeleine Thomas, Golder Associates Pty Ltd	WE13 MINE SITES – MANAGING THE NEXUS BETWEEN ACTIVE MINE SITES AND CONTAMINATED LAND PHILOSOPHY Tim Chambers, Environmental Strategies	WF13 ENHANCING RISK COMMUNICATION: IDENTIFYING INTEGRATION MECHANISMS BETWEEN EMPIRICAL SCIENCE, SOCIAL SCIENCE AND THE HUMANITIES Kathryne T. Hughes, University of Technology Sydney
WD14 SOIL CONTAMINATION AMD RISK ASSESSMENT AT HOUNSLOW HEATH EX-LANDFILL SITE IN LONDON, UK John L Zhou, University of Technology Sydney	WE14 UTILIZATION OF BIOWASTES FOR MINE SPOILS REHABILITATION Hasintha Wijesekara, University of South Australia	WF14 ENVIRONMENTAL AND SOCIETAL MANAGEMENT OF CONTAMINATED LAND IN NIGERIA: THE NEED FOR POLICY AND GUIDANCE CHANGES Kabari Sam, Cranfield University
MORNING TEA		

	CONFERENCE HALL 1 (CCH1)	CONFERENCE HALL 2 (CCH2)	CONFERENCE HALL 3 (CCH3)
11:10 – 12:50	**WA2 Climate change and remediation – Presentations** **Chair: Vanessa Bryant, Ramboll Environ** **Sponsor: Ramboll Environ**	**WB2 Fractured rock sites** **Chair: Grant Carey, Porewater Solutions** **Sponsor: Geosyntec**	**WC2 Per-fluorinated compounds** **Chair: Peter Storch, EHS-Support Pty Ltd**
11:10	WA21 THE INFLUENCE OF CLIMATIC UNCERTAINTY ON GROUNDWATER RESTORATION METHODS Scott Warner, Ramboll Environ	WB21 NATURALLY OCCURRING ABIOTIC DECHLORINATION OF TCE IN ROCK MATRICES Charles Schaefer, CDM Smith	WC21 PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOIC ACID (PFOA): ECOTOXICITY AND ENVIRONMENTAL CONCERNS Megharaj Mallavarapu, University of Newcastle
11:30			WC22 INNOVATIVE TECHNOLOGIES ON TREATING PERFLUOROALKYL SUBSTANCES Dora Chiang, AECOM
11:50	WA22 SEA LEVEL RISE AND CONTAMINATED SITES – MORE CHALLENGES AND HARD DECISIONS LIE AHEAD Paul van der Beeke, Golder Associates Pty Ltd	WB22 DISTRIBUTION OF VEGETABLE OIL-BASED SUBSTRATE TO REMEDIATE SHALLOW FRACTURED BEDROCK UNDER SAPROLITIC CONDITIONS Mike Sieczkowski, JRW Bioremediation	WC23 C6 SHORT-CHAIN FLUOROTELOMERS PROVIDE A BETTER ENVIRONMENTAL SOLUTION AND SUPERIOR PERFORMANCE FOR CLASS B FIREFIGHTING FOAM APPLICATIONS Mike Willson, Willson Consulting
12:10	WA23 GROUNDWATER MONITORING & REMEDIATION UNDER CHANGING CLIMATE CONDITIONS Tamie Weaver, ERM	WB23 HIGH RESOLUTION SITE CHARACTERIZATION: CHLORINATED SOLVENT CONTAMINATION IN POROUS SEDIMENTARY ROCK Seth Pitkin, Stone Environmental	WC24 PFOS AND PFOA: SCREENING CRITERIA AND WHAT HEALTH INVESTIGATION LEVELS MIGHT LOOK LIKE Giorgio De Nola, Cardno
12:30	WA24 THE IMPLICATIONS OF CLIMATE CHANGE FOR SITE ASSESSMENT, MANAGEMENT AND REMEDIATION Stella Whittaker, Ramboll Environ	WB24 FRACTURED ROCK BIOREMEDIATION CROSS ROADS: NEW MILLENNIUM MICROBIOLOGY VS LAST CENTURY HYDROGEOLOGY David Major, Savron	WC25 ENVIRONMENTAL FACTORS AFFECTING THE SELECTION AND USE OF FIRE-FIGHTING FOAMS – A FIRE SAFETY PERSPECTIVE Brett Staines, UTC Building and Industrial Systems
12:50 – 13:40	**LUNCH**		

MEETING ROOM 11 (M11)	MEETING ROOM 12 (M12)	MEETING ROOM 13 (M13)
WD2 Nanotechnology for groundwater remediation **Chair: Volker Birke, Ostfalia University of Applied Sciences**	**WE2 Mine site remediation, revegetation and rehabilitation** **Chair: Ravi Naidu, CRC CARE**	**WF2 Advances in waste treatment and management** **Chair: Warren Pump, ERM**
WD11 ZERO-VALENT IRON MATERIALS FOR ENVIRONMENT RESTORATION – A RELOOK AT THE UNMODIFIED, CATALYZED, AND SULFIDED IRON Weile Yan, Texas Tech University	WE21 REHABILITATION FUTURES FOR COALMINES IN THE HUNTER VALLEY Dee Murdoch, AECOM	WF21 IS SEGREGATION OF BONDED ASBESTOS FROM SOIL CHEAPER THAN DIG AND DUMP REMEDIAL METHODS? –REMEDIATION OF ASBESTOS IMPACT IN UNCONTROLLED FILL IN URBAN NSW – A CASE STUDY James Boyle, Coffey Environments
		WF22 THE THERMAL BEHAVIOUR OF RED MUD DURING HEAT TREATMENT Yanju Liu, University of Newcastle
WD12 EVALUATING THE MOBILITY OF POLYMER-STABILISED ZERO-VALENT IRON NANOPARTICLES (NZVI) Laura Chekli, University of Technology Sydney	WE22 RISK ASSESSMENT AND MANAGEMENT OF DERELICT MINES IN NSW David Blackmore, Department of Industry-Resources and Energy	WF23 CHEMICAL PROPERTIES OF SEAWATER NEUTRALIZED RED MUD IN RELATION TO REVEGETATION Eileen Li, University of Queensland
WD13 DEGRADATION OF MALATHION BY BI-METALLIC FE-NI NANOPARTICLES GRAFTED ON PALYGORSKITE Binoy Sarkar, University of South Australia		WF24 REMEDIATION OF COMPLEX HAZARDOUS WASTES: HISTORICAL AND EMERGING CONTAMINANTS Annette Nolan, Enviropacific Services
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LESS IS MORE: AN EFFICIENT APPROACH TO IN SITU SOURCE TREATMENT USING ACCELERATED BIOREMEDIATION

Eric Kern

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In situ bioremediation is a well-established remedial technology for source treatment of chlorinated volatile organic compounds (VOCs) in groundwater. The technology can be used singularly, or incorporated as an element of a broader remedial strategy, to shorten the life cycle of a groundwater treatment program. The success of the treatment technology is contingent upon development of a sound site conceptual model, which entails a comprehensive understanding of site geochemistry, geology, hydrogeology, risk management, and regulatory objectives.

The design of an effective bioremediation program involves a fundamental understanding of microbial reductive dechlorination processes harmoniously paired to the site hydrodynamic conditions that govern amendment distribution. The goal is to support efficient and complete reductive dehalogenation of chlorinated VOCs by achieving broad distribution of relatively low concentrations of electron donors throughout the treatment area.

This presentation focuses on key design considerations related to amendment composition and concentration that influence the ability to achieve optimal concentrations of amendments within a treatment area to support efficient microbial reductive dechlorination processes.

MOLECULAR BIOLOGICAL TOOLS TO IDENTIFY AND OVERCOME OBSTACLES TO SOURCE ZONE BIOREMEDIATION AT COMPLEX SITES

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INTRODUCTION

With converging degradation pathways, preferential electron acceptor utilization, and potential inhibition issues, complex sites impacted by mixtures of chlorinated ethenes, ethanes, and methanes pose unique challenges. In the current study, quantitative polymerase chain reaction (qPCR) were combined with traditional groundwater monitoring to assess the feasibility and performance of anaerobic bioremediation of a fractured basalt aquifer impacted by tetrachloroethane, 1,1,2-trichloroethane (TCA), 1,2-dichloroethane (DCA), and chloroform. Biological dechlorination processes had occurred historically, but substantial populations of *Dehalococcoides*, *Dehalobacter*, and *Dehalogenimonas* spp. were only detected in part of the source area indicating that biostimulation was needed. Propylene glycol (PG) was injected as an electron donor to enhance anaerobic biodegradation. Across most of the treatment zone, decreases in parent compound concentrations were accompanied by daughter production formation and increases in populations of organohalide respiring bacteria. The lone exception was a distinct area of a former chlor-alkali plant where high concentrations of chloroform appeared to limit growth *Dehalococcoides*. A groundwater recirculation and biostimulation system was implemented to overcome chloroform inhibition in this area and promote long-term biodegradation of vinyl chloride.

METHODS

In 1969 a major grassfire at the site destroyed a storage area holding liquid chlorinated byproducts from the manufacture of DCA resulting in groundwater contamination. Over 200 tons of a 50% propylene glycol (PG) solution have been injected at the site to promote anaerobic bioremediation. For biostimulation in the inhibited area, groundwater is extracted from a downgradient pumping well and reinjected just upgradient of the inhibited area. Intermittently, the recirculated water is amended to 25% (w/v) propylene glycol and buffered with potassium bicarbonate. To date, a total of 9000 m^3 of downgradient groundwater has been extracted and reinjected. Throughout the project, qPCR and QuantArray analyses were performed with groundwater samples obtained from across the site to quantify known halorespiring bacteria and functional genes (vinyl chloride, DCA, and chloroform reductases) to treatment performance.

RESULTS AND DISCUSSION

Site Characterization and Biostimulation

During site characterization, low concentrations of *Dehalococcoides* and reductive dehalogenase genes but moderate populations of *Dehalobacter* and *Dehalogenimonas* spp. suggested that the observed production of vinyl chloride and ethene were due to dichlorelimination of TCA and DCA rather than biodegradation of chlorinated ethenes.

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Following PG, increases in malorespiring populations and functional genes were accompanied by decreases in concentrations of chlorinated ethanes, isotopic enrichment of TCA and DCA, and the near stoichiometric production of vinyl chloride and ethene.

Statistical Analyses

One-way ANOVA revealed that reaching volatile fatty acid (VFA) concentrations greater than 1,000 mg/L and driving sulfate concentrations below 50 mg/L were critical in achieving *Dehalococcoides* populations greater than 10^4 cells/mL. Near the outfall of the former chlor-alkali plant, chloroform inhibited growth of halorespiring bacteria despite electron donor availability and appropriate geochemical conditions.

Overcoming Inhibition

After targeted recirculation and continued biostimulation in the inhibited area, *Dehalococcoides* populations increased substantially and were greater than 10^4 cells/mL in nearly all of the monitoring wells located in the formerly inhibited area. Moreover, vinyl chloride reductase gene copies increased by an average of three orders of magnitude and were greater than the operating target of 10^3 gene copies/mL in nearly all of the wells influenced by the system (Fig. 1). The positive impact of system operations extended downgradient promoting growth of halorespiring bacterial populations in off-site locations.

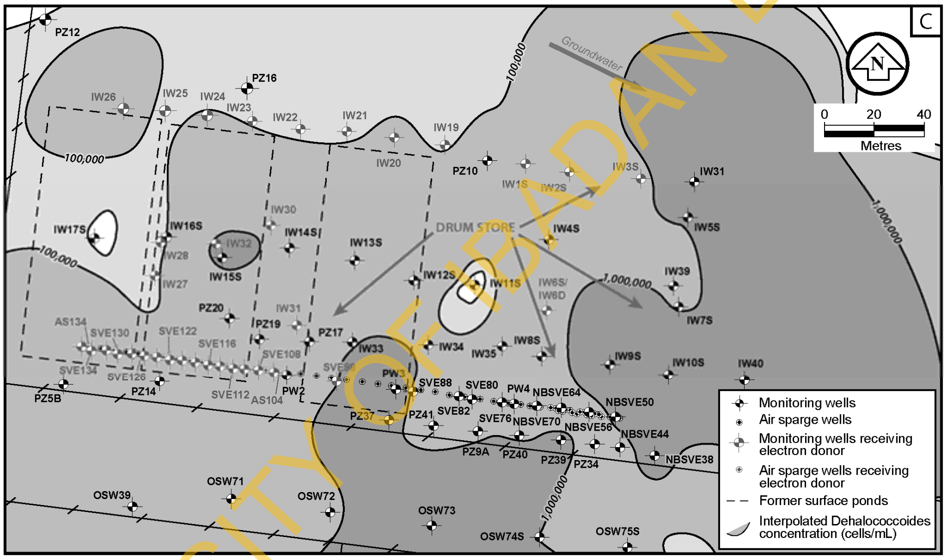

Fig. 1. Site map depicting *Dehalococcoides* concentrations exceeding 10^4 cells/mL through the source area after biostimulation and targeted recirculation to overcome chloroform inhibtion.

CONCLUSIONS

Propylene glycol was a very effective electron donor for stimulating reductive dechlorination of chlorinated ethanes and ethenes. Statistical analysis indicated that *Dehalococcoides* populations greater than the 10^4 cells/mL target concentration could be achieved by PG injections resulting in VFA concentrations greater than 1,000 mg/L and driving sulfate concentrations below 50 mg/L. Chloroform at concentrations of 4 to 5 mg/L limited growth of *Dehalococcoides* and *Dehalogenimonas* spp. However, targeted recirculation and continued biostimulation overcame chloroform inhibition. Routine qPCR and QuantArray analysis of *Dehalococcoides*, *Dehalobacter*, *Dehalogenimonas* spp. and a variety of reductive dehalogenase genes provided a key line of evidence in site assessment and evaluation of treatment performance. Notwithstanding the challenges of a complex site impacted by a mixture of contaminants, the chemical, geochemical, and microbial lines of evidence conclusively demonstrated enhanced bioremediation in response to site management activities.

UNRAVELLING MICROBIAL BIOREMEDIATION OF ORGANOPHOSPHATES: A METAGENOMIC SYSTEMS-BIOLOGY APPROACH

Thomas C. Jeffries, Smriti Rayu, Ali Z. Ijaz, Brajesh K. Singh

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INTRODUCTION

The growing extent of contaminated land and water due to industrialization is a major global concern and the remediation of contaminated sites is a key goal of a sustainable future. Organophosphate (OP) compounds represent a major environmental contaminant due to their role as a nerve agent and thus widespread application as pesticides. In addition to acute toxicity to humans, which results in over a million poisonings annually, chronic exposure to these compounds may lead to long term neurological and developmental effects (Singh, 2009). Microbial bioremediation of toxic compounds often suffers from a lack of understanding of the types and roles of degrading bacteria within the context of the diverse community and ecological drivers present in the system. New genomic technologies are leading to a more holistic understanding which synthesizes information regarding the organisms present, functional gene abundances and environmental variables.

METHODS

Here we have used shotgun metagenomics to profile microbial communities from agricultural soils across a gradient of OP insecticide usage and varying in their ability to degrade OP compounds *In Situ*. Whole community DNA was extracted from soil samples collected from sugar cane plantations in conjunction with OP pesticide levels and environmental variables. DNA was sequenced using Illumina technology and both the taxonomic and metabolic profiles of microbial communities was reconstructed using the MG-RAST metagenomics pipeline (Meyer et al, 2008) and a custom entropy based annotation pipeline for taxonomic marker genes. The Statistical Analysis using Metagenomic Profiles (STAMP) software package (Parks et al, 2014) was used to elucidate organisms and genes related to OP degradation which were incorporated into a predictive co-occurrence network model using Cytoscape (Shannon et al, 2003).

RESULTS AND DISCUSSION

We found that the major determinant of both taxonomic composition and genomic functional potential was a site history of insecticide usage, with contaminated samples being dominated by *Actinomycetales, Burkholderiales, Myxococcales and Rhizobiales* bacterial groups. Shifts between contaminated and uncontaminated soils were driven by an increase in genes related to phosphorus metabolism, membrane transport, stress response and chemotaxis. These metabolisms were also found to increase in abundance after the addition of OP insecticide to laboratory samples which previously had low concentrations of these compounds and which displayed OP degradation, indicating their role in the microbial response to OP contamination and in OP degradation. By applying network analysis to this dataset, we have built a model that links key taxa to OP degrading genes within a wider metabolic network to elucidate the consequences of organophosphate pesticide on microbial function and degradation.

CONCLUSIONS

Using this systems-biology approach we have developed a model to predict strategies which encourage the degradation of contaminants *In Situ.* These models will help expedite bioremediation of contaminated sites and facilitate the development of predictive tools to aid practitioners in choosing the optimal bioremediation strategy based on the specific microorganisms present

ACKNOWLEDGEMENTS

We acknowledge funding for this project by CRC-CARE.

REFERENCES

Singh, B.K. (2009) Organophosphorus-degrading bacteria: ecology and industrial applications. *Nat. Rev. Microbiol*. 7: 156-164

Meyer, F., Paarmann, D., D'Souza, M., Olson, R., Glass, E. M., Kubal, M et al. (2008) The metagenomics RAST server–a public resource for the automatic phylogenetic and functional analysis of metagenomes. *BMC Bioinformatics*, 9:386.

Parks, D. H., Tyson, G. W., Hugenholtz, P., & Beiko, R. G. (2014). STAMP: statistical analysis of taxonomic and functional profiles. *Bioinformatics*, 30: 3123-3124.

Shannon, P., Markiel, A., Ozier, O., Baliga, N. S., Wang, J. T., Ramage, D.et al. (2003) Cytoscape: a software environment for integrated models of biomolecular interaction networks. *Genome research*, 13: 2498-2504.

BIOREMEDIATION OF WEATHERED HYDROCARBON CONTAMINATED CLAY SEDIMENTS

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INTRODUCTION

In Australia, the redevelopment of contaminated land and the necessity to reuse remediated soils is likely to become more prevalent in addition to other drivers for site clean-up. As with several of the other nations, Australia has truly kept up predominance towards the excavation and disposal of contaminated soils to landfill when remediating contaminated sites. This methodology is unsustainable, both as far as waste to landfill, the carbon footprint associated with such practise and utilization of non-remediated materials in lieu of remediated materials. The tonnage of contaminated soils to landfill is annually distorted by any particular major development occurring in that given year.

The application of sustainability principles in the context of contaminated land management and remediation is widely encouraged around the world. Australian regulatory authorities have also shown growing support for the principles of sustainability in contamination management, driven largely by the adoption of green remediation approaches to contamination issues. In this study, we attempted to apply various green remediation methods to clean the hydrocarbon contaminated clay sediments from an oily wastewater lagoon. Due to the severity of the hydrocarbon concentration, the alternate option for the resource industry was to incinerate which will significantly increase the environmental footprints.

METHODS

Contaminated sediments

The hydrocarbon contaminated sediment collected from various depths from a single evaporation pond in the oily wastewater lagoon at a mining site in Western Australia. The sludge was highly hydrophobic and greasy nature. Sediment was characterised comprehensively, total petroleum hydrocarbons (TPH) concentration and microbial diversity were the two important characters considered for development of the remediation strategy.

Feasibility study with ^{14}C-hexadecane

In the preliminary experiment, 2 groups of microcosms were set up to evaluate the feasibility of biopile and bioslurry techniques in removing weathered hydrocarbons. One group was a without surfactant, the other group was experimented with the addition of either Triton X100 or Alkyl Poly Glycoside (APG) @ 2% to enhance the solubility of the weathered hydrocarbons. In this microcosm study, ^{14}C labelled hexadecane was utilised as a model compound to monitor potential microbial degradation of the contaminated sediment. Utilising ^{14}C labelled hexadecane allowed a rapid assessment of the model compound microbial degradation rate. The addition of the surfactants Triton X100 and APG increased TPH solubility which increased microbial TPH bioavailability. However triton is a complex surfactant, not co-degraded along with TPH and therefore leaving a secondary pollutant which is a concern. Hence bioslurrying with APG is preferred for the pilot scale study to improve the remediation process.

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Pilot scale bioslurry bioreactor with green surfactant APG

Based upon the microcosm results, pilot scale bioslurry treatment trials were conducted with large quantity of clay sediments. About 80 kg of unprocessed (wet and un-sieved) TPH contaminated sediment was placed in the bioslurry reactor to which nutrients were added. The rate of nutrient addition was calculated based on a TPH sediment concentration of 30000 mg kg^{-1} to achieve a chemical (mole) ratio of 100:10:1 for C:N:P. Approximately 120 l of reticulated water containing 2% (v/v) APG was added to the contaminated sediment @ solid: solution ratio of 1:3. Samples of the slurry and the water were collected from day 1 through to day 80 and TPH concentration was monitored. The slurry phase pH and surface tension was measured and maintained continuously.

RESULTS AND DISCUSSION

TPHs in raw sediment ranged from 23208 ± 1699 to 41228 ± 128 mg TPH kg^{-1}(dry weight). Pre-screening assay and microcosm ^{14}C-hexadecane studies indicated that bioremediation through biopiling may not be feasible without considerable modification of the contaminated sediment environment. Non-ionic Alkyl Poly Glycoside (commercially available plant extract often utilized in the pharmaceutical industry) effectively solubilized the recalcitrant TPH (Han et al. 2009) in the sediments and selected as the best amendment for the next phase large scale pilot study. Pilot scale bioslurry treatment of contaminated sediments with APG showed that TPH concentration in sediment decreased from 15000 to 6000 mg kg^{-1} after 70 days of treatment. Continued bioslurry treatment showed that the TPH sediment fall below the respective ecological guideline value after approximately 80 days of treatment. The TPH concentration in the aqueous phase (Slurry) fell from nearly 5000 mg L^{-1} to 750 mg L^{-1} during the same treatment period.

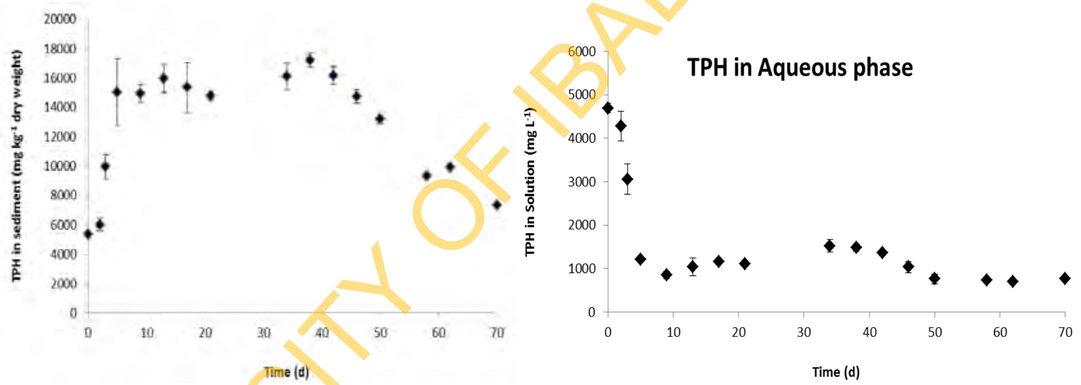

Fig. 1. TPH biodegradation in sediment and slurry phase

CONCLUSIONS

This case study provides a highlight of the real field application of green remediation approaches in cleaning up weathered hydrocarbon contaminated clay sediments. Significant opportunities exist to increase sustainability of site remediation while helping to meet national, regional, and state or local goals regarding natural resource conservation and climate change. Site-specific strategies must take into account the unique challenges and characteristics of a site; no single solution exists. At all sites, however, key opportunities for integrating core elements of green remediation can be found when designing and implementing clean-up measures. Decision-makers are encouraged to take advantage of newly demonstrated or emerging technologies by CRC CARE in ways that creatively meet the objectives of site clean-up as well as revitalization.

REFERENCES

Illaszewicz J. and Gibson K. (2009) Green and sustainable remediation: Creating a framework for environmentally friendly site cleanup. Env. Quality Mgmt 18:1-8.

Han M. Ji G. and Ni J. (2009) Washing of field weathered crude oil contaminated soil with an environmentally compatible surfactant, alkyl polyglucoside Chemosphere 76:579-586.

IN SITU BIOREMEDIATION OF CHLORINATED SOLVENT SOURCES

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INTRODUCTION

In situ bioremediation (ISB) was not initially considered a feasible technology for treating chlorinated solvent source zones, and it still faces some skepticism. However, experience over the last decade demonstrates that it is a viable technology for treating some source zones. However, realistic objectives must be set. It is reasonable to expect 90-99% reductions in groundwater concentrations and mass discharge from a source in many situations, but it is not likely that ISB can achieve complete cleanup of a source zone within a few years. ISB is best applied in stages, optimizing the design and operations over time. Some residual contamination may remain, and modeling suggests that contaminant concentrations may rebound after treatment, although few cases of rebound have been observed so far at field sites. Recent evidence suggests that the accumulation of biomass and reduced minerals during ISB will sustain treatment for several years after active treatment ends.

This presentation will focus on practical considerations that site managers considering ISB for a source zone should understand. In particular, treating a source can require adding large amounts of electron donor demand, which may not be feasible, and it may also require adding large amounts of pH buffer, which can be costly or even impractical. Adding large amounts of donor may also cause other problems, such as methane production, biofouling of wells, or clogging of the subsurface, so using ISB to treat source zones requires careful design, monitoring and continuous optimization throughout treatment. Finally, it is likely that some contaminant mass will remain, and the area may require extended passive management after treatment.

Three case studies will be briefly summarized to illustrate the performance and issues associated with ISB of source zones at a field scale. The case studies demonstrate ISB through both active treatment (recirculating electron donor through the treatment area) and passive treatment (infrequent donor injections without recirculation). All demonstration projects have been in unconsolidated media with DNAPL present, consisting of perchloroethene (PCE) and/or trichloroethene (TCE), and have been carefully characterized and monitored to evaluate both the removal that can be achieved and the post-treatment conditions.

FUTURE DEVELOPMENTS

In situ bioremediation for chlorinated ethenes is a rapidly evolving technology, especially when applied to source zones. Source-zone treatment in general has gained acceptance and developed a record of experience only over the last decade. The next decade is likely to see refinement of the approaches taken, applications of the basic principles to more complex sites, more cost-effective monitoring and operation, and deliberate combinations with other technologies, sequentially or simultaneously. Key needs for future applications include:

1) **Improved Understanding and Treatment of Low-Permeability Regions**
   Understanding if targeted treatment of lower-permeability zones is needed, and then designing cost-effective ways to treat these zones, are important issues for ISB. Like any injection-based strategy, most of the amendments move through and remain in the most transmissive regions. One potential approach to improving delivery is to co-inject the amendments with shear-thinning agents (such as gum agar), to temporarily clog the

transmissive regions and force amendments into the less permeable areas. Another possibility is to combine ISB or ISCO or ISCR with electrokinetics (EK) to improve amendment delivery to the low-permeability zones.

2) **Improving Delivery to DNAPL Accumulations**
The difficulty of delivering water-soluble electron donors to the DNAPL phase is obvious, and makes effective treatment of sites with DNAPL accumulations very challenging. One solution is the use of partitioning electron donors (organic compounds such as *n*-butyl acetate and *n*-hexanol that can be delivered in water but can partition into the DNAPL phase). Another is to inject vegetable oils, so that the chlorinated solvent partitions into the oil droplets, forming a mixed NAPL that will provide both electron donor and electron acceptor for bacterial growth.

3) **ISB at Fractured Rock Sites**
DNAPL sources located in bedrock are particularly difficult to treat and manage. It is difficult to characterize the DNAPL nature and extent, matrix storage can sustain plumes for decades, and delivering amendments can be very challenging. Laboratory research has indicated that bioaugmentation can be highly effective in enhancing the removal of DNAPL from fractures within bedrock, and limited field testing also has suggested that bioaugmentation can be effective in bedrock. There is a need for well-monitored field-scale demonstrations to understand the costs and performance, and for improvements in the technology to increase the use of ISB at fractured bedrock sites.

4) **Long-Term Performance Predictions and Improvements**
ISB treatment in DNAPL source zones generally must be sustained over several years in order to achieve significant mass reductions. However, there is still uncertainty regarding the long-term performance. For example, what will be the post-treatment equilibrium state, and how long will it take before re-equilibration occurs? Modeling results suggest that ISB may have relatively little effect on the total source mass and the mass discharge from the source several years after treatment is stopped, as compared to natural dissolution of the source zone, and that the greatest long-term enhancement will be in heterogeneous and low-permeability aquifers. There will almost certainly be some remaining mass within the source zone after ISB is terminated, and this remaining source mass can sustain plumes for decades above regulatory criteria. Validated models can help determine the need for monitoring and its frequency, better long-term monitoring methods will reduce the costs, and materials may be developed specifically to ensure long-term treatment.

REFERENCES AND RESOURCES

ITRC. 2008. In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones. ITRC, Bioremediation of DNAPLs Team, Washington, DC, USA. http://www.itrcweb.org/Documents/bioDNPL_Docs/BioDNAPL3.pdf.

Sale T, Newell C, Stroo H, Hinchee R, Johnson P. 2008. Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater. ESTCP, Arlington, VA, USA. http://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/DNAPL-Source-Zones.

Stroo HF, MR West, BH Kueper, RC Borden, DW Major, and CH Ward. 2014. *In Situ* Bioremediation of Chlorinated Solvent Sources. Chapter 12 (Pages 395-457) In Kueper BK, HF Stroo, C Vogel, CH Ward (Editors). Chlorinated Solvent Source Zone Remediation. Springer, New York, NY. 716 p.

Stroo HF, A Leeson, JA Marqusee, PC Johnson, CH Ward, MC Kavanaugh, TC Sale, CJ Newell, KD Pennell, CA Lebrón, and M Unger. 2012. Chlorinated ethene source remediation: Lessons learned. Environmental Science & Technology 46:6438−6447. Available at: pubs.acs.org/doi/full/10.1021/es204714w.

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FULL SCALE BIOREMEDIATION OF TRICHLOROETHENE

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INTRODUCTION

A large, multi-year, full-scale bioremediation program to treat Trichloroethene (TCE) impacts in groundwater in a complex fractured basalt environment is being undertaken in Victoria, Australia. The results after 2.5 years have indicated molar reduction of chlorinated ethenes and reductive dechlorination of trichloroethene to ethene in groundwater in, and downgradient of the treatment area.

BACKGROUND / METHODS

TCE was measured in groundwater at up to 130 mg/L prior to treatment. The pre-treatment groundwater conditions were not favourable for anaerobic microbial reductive dechlorination of TCE.

The approach to remediation involved the pressure injection of zero valent iron- or carbon-based amendments into injection wells across three injection events, with monitoring for indicators of TCE degradation and water quality parameters. The amendment mixtures were prepared using groundwater that had been previously bioaugmented with a microbial culture containing reductively dechlorinating bacteria. The 4600 m^2 treatment area includes over 100 injection wells that target groundwater around 10 m below ground level in an about 4 m thick section of variably fractured basalt that occurs between two clay palaeosols.

RESULTS AND DISCUSSION

Concentration reduction and transformation of chlorinated ethenes was recorded in monitoring wells in the treatment area, and in selected wells downgradient of the treatment area (refer to Fig. 1).

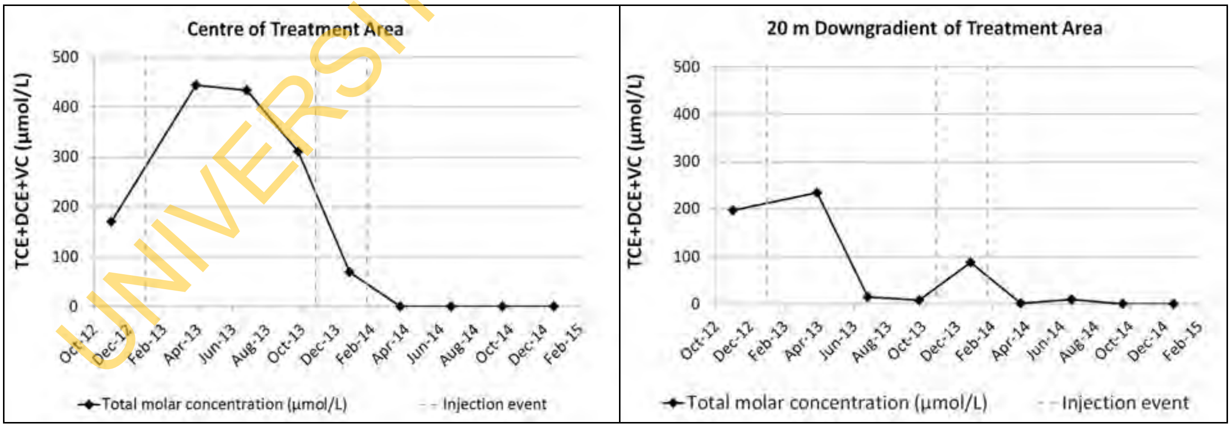

Fig. 1. Total Molar Concentration of the Key Chlorinated Ethenes in Monitoring Wells In and Downgradient of the Treatment Zone

There was evidence of complete reductive dechlorination in the treatment area (refer to Fig. 2). Ethene was recorded in monitoring wells in the treatment area, and in selected wells downgradient of the treatment area. The results have not indicated a stall in the reductive dechlorination of TCE at dichloroethene or vinyl chloride.

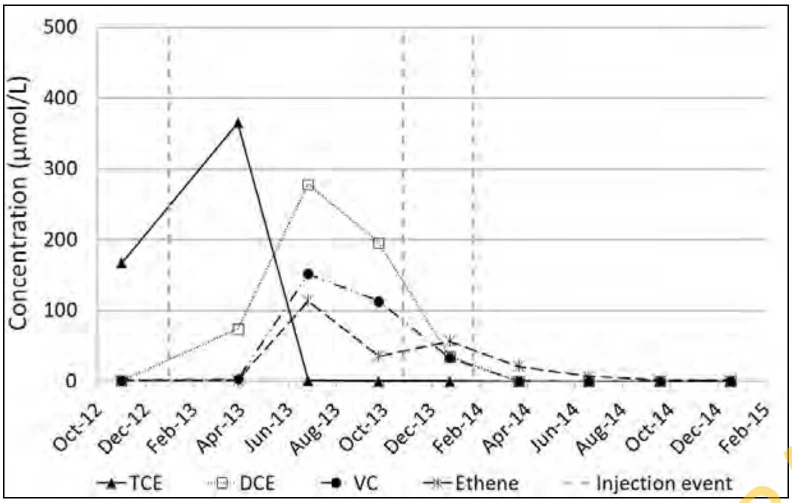

Fig. 2. Key Chlorinated Ethenes in the Treatment Area

Monitoring for ongoing trends continues. This monitoring includes testing for evidence of rebound in the concentration of TCE and other chlorinated ethenes as amendment sources in the treatment area are depleted and the water quality returns to pre-treatment conditions.

CONCLUSIONS

Concentration reduction and conversion of chlorinated ethenes was recorded in monitoring wells in a treatment area of 4600 m^2 and about 4 m thickness. Wells downgradient of the treatment area are now showing similar trends indicating that the mass reduction is also influencing downgradient contaminant concentrations and mass flux in the dissolved phase plume. Monitoring for ongoing trends continues.

ACKNOWLEDGEMENTS

This project was performed in collaboration with Orica Australia Pty Ltd. Golder thanks Orica for the opportunity to participate in this project.

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MODELLING NATURAL ATTENUATION PLANNING RELIABILIY BY A LONG TERM PROGNOSIS?

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INTRODUCTION

The soil and groundwater contamination in the southern city of Hannover, Germany, consists mainly of chlorinated volatile organic carbon (CVOC). It is well known that since 1976 large amounts of different substances have accessed the subsurface on the premises of a former chemical wholesale company. Due to extensive groundwater abstraction linked to a period of subway construction in the seventies and eighties the contaminant transport was accelerated and spread out due to the moving focus of abstraction. Nowadays the plume extends over wide parts of the southern city of Hanover. During the years 1988 to 1993, the City of Hanover had started a hydraulic remediation of the pollutant plume, however without any major success. The source area had been safeguarded by 1993. Within the framework of the BMBF funding priority "KORA" between 2003 and 2007 a slow, a continuous decrease of the contamination was proven by detailed groundwater monitoring. Natural degradation of the contaminants is obviously taking place in separate zones. From 2007 till now the ongoing degradation process was monitored in 105 observation wells and compared to results of a complex groundwater and solute transport model.

The objective is to provide model results on the further development of the remaining contaminant mass and concentrations of individual compounds. The central question is whether model predictions for a long time period, with constantly changing boundary conditions in the setting of an active city can provide helpful results for future planning?

Table 1. Decrease of dissolved CVOC mass in groundwater due to natural attenuation.

Year	TCE [kg]	cDCE [kg]	VC [kg]	∑ CVOC [kg]
2004	100	1.200	800	2.100
2005	100	1.100	800	2.000
2006	100	1.000	700	1.800
2009	225	800	450	1.475
2014	66	662	118	846

METHODS

Within the framework of the KORA funding priority a groundwater and reactive transport model was developed, which represented the complex three dimensional degradation conditions of the southern city of Hanover. The concept model describes this system. It takes into consideration all metabolites of perchloroethene. For cDCE and VC the aerobic as well as stepwise anaerobic dechlorination are being considered. Different degradation zones are being defined. The contaminant sorption resp. desorption is described by an in-stationary two-site sorption approach. For the model calibration comprehensive monitoring results were available over a period of 10 years. The model was validated at the monitoring campaign 2006, 2009. By comparison with monitoring results obtained in 2015 it is now being examined whether the chosen model approach remains valid and whether a long-term forecast up to reaching the regulatory remediation target concentration is justified.

RESULTS AND DISCUSSION

Compared to dissolved CVOC concentrations (2015) we can see that the model predictions are still valid after a forecast period of 10 years (see fig. 2). The remaining dissolved CVOC mass (monitoring 2015) in the contaminant plume has been predicted very accurately (deviation < 5%) with the model approach. This is all the more astonishing as the desorbtion of sorbed CVOC has a significant impact on the fate of the contaminant plume. Deviations for individual metabolites are higher. Small changes in the geochemical milieu demonstrably lead to changes of the degradation rates.

The forecast of contaminant concentrations for individual wells in the forecast period is only possible to a limited extent. Overall it can be summarized that the given remediation objective concentration of < 250 µg/l ∑ CVOC is expected to be attained by the year 2015 for the entire contaminant plume.

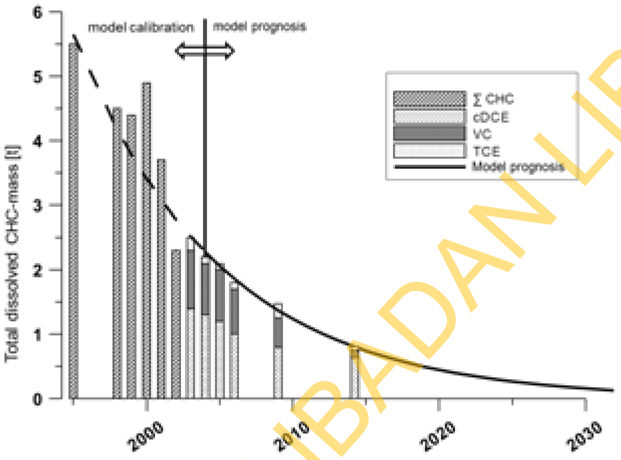

Fig. 2: Development of mass of CHC metabolites: prediction and measurement.

CONCLUSIONS

It can be shown that a long-term model-based prediction for natural degradation processes until reaching the remediation target values is possible with sufficient precision. Hereby numerical model calculations are an instrument which can provide authorities with sufficient planning security for the later use of contaminated groundwater areas. For valid, detailed and long-term prediction of the contamination development certain conditions must be fulfilled: extensive time series of metabolite concentration must be available coupled with a detailed process understanding including geochemical and microbiological transformation as a result of site specific investigations must be set up. Nevertheless, an accurate knowledge and forecast of natural attenuation is far more cost-saving than active remediation measures.

REFERENCES

Wegner, M., Wieschemeyer, M., Hoffmann and S., Kringel, R. (2009): A pilot project of a successful Application of Natural Attenuation: Groundwater Chlorinated Hydrocarbons Contamination in Hannover, Germany, presentation on 3rd clean up conference, Adelaide

ENHANCEMENT OF BIODEGRADATION OF 1,1,1-TCA AND 1,1-DCA BY THE INJECTION OF EVO AND NUTRIENTS

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INTRODUCTION

1,1,1-Trichloroethane (1,1,1-TCA) was produced in large quantities as an industrial solvent. It is being phased out following its identification in the Montreal Protocol as an ozone depleting substance but its historic production leaves a legacy of groundwater contamination. which is similar to what we have seen in Australia as well. 1,1,1-TCA is less readily oxidizable than chlorinated ethenes such as trichloroethene (TCE) and is often difficult to treat using in situ chemical oxidation (ISCO). However, 1,1,1-TCA can be degraded by reductive dechlorination where it is used as an electron acceptor by bacteria. Previously, success in treatment of 1,1,1-TCA using enhanced biodegradation has been inconsistent.

A large site in the United States required treatment of historic groundwater contaminated with 1,1,1-TCA as well as other chlorinated solvents. A laboratory treatability study was performed to determine the parameters for field scale enhancement of biodegradation. A field pilot study was then performed to test the selected technology at the field scale. This complements our experience in treating dense non aqueous phase liquid (DNAPL) contaminated groundwater in Australia where field pilot trials were conducted using similar and other remediation technologies.

METHODS

The laboratory treatability study was performed using soil and groundwater collected from the site. Microcosms were set up that received different amendments. Microcosms were sacrificed and analysed after 4, 8, and 12 weeks.

For the field pilot study EVO and nutrients were injected into three wells. Each injection well had three monitoring wells clustered around it to monitor the effects of the injection. Quarterly monitoring was performed.

RESULTS AND DISCUSSION

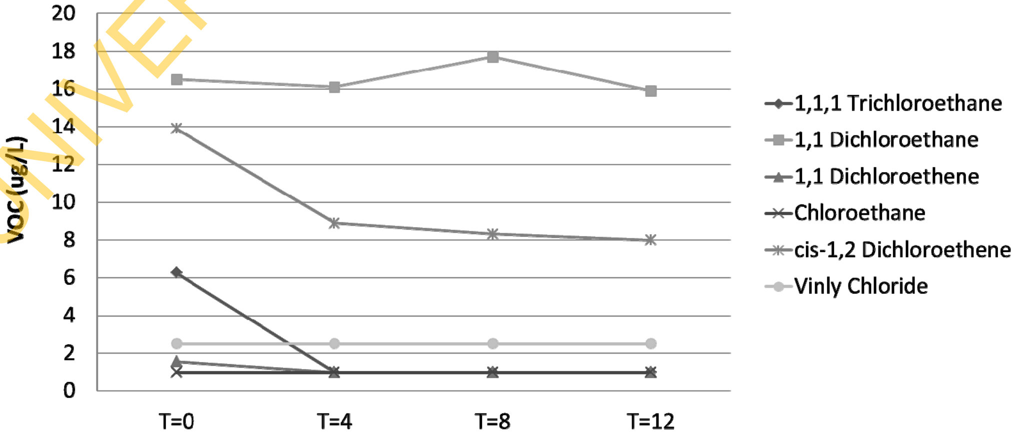

Figure 1. Treatability Study Results from Microcosms that Received EVO and Nutrients

The results of the treatability study showed that the addition of emulsified vegetable oil (EVO) and nutrients were required to stimulate biodegradation but that the addition of a microbial inoculum was not required.

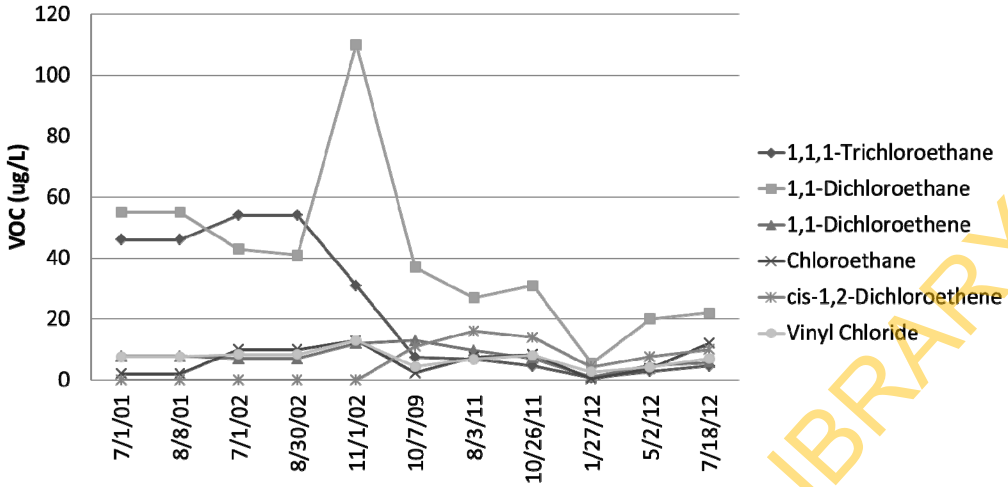

Figure 2. Volatile Organic Compounds over Time in the Pilot Test

After the field pilot test injections, monitoring results showed decreases in 1,1,1-TCA in all the wells where it was initially present. Increases in the 1,1,1-TCA daughter products 1,1-dichloroethane (1,1-DCA) and chloroethane were observed during the earlier monitoring events however they had decreased by the final monitoring event at most wells. The presence of ethane and ethene in all wells confirmed that complete biodegradation to non-chlorinated end products was occurring. PCR analysis of dechlorinating bacteria showed that populations of these bacteria increased during the pilot study.

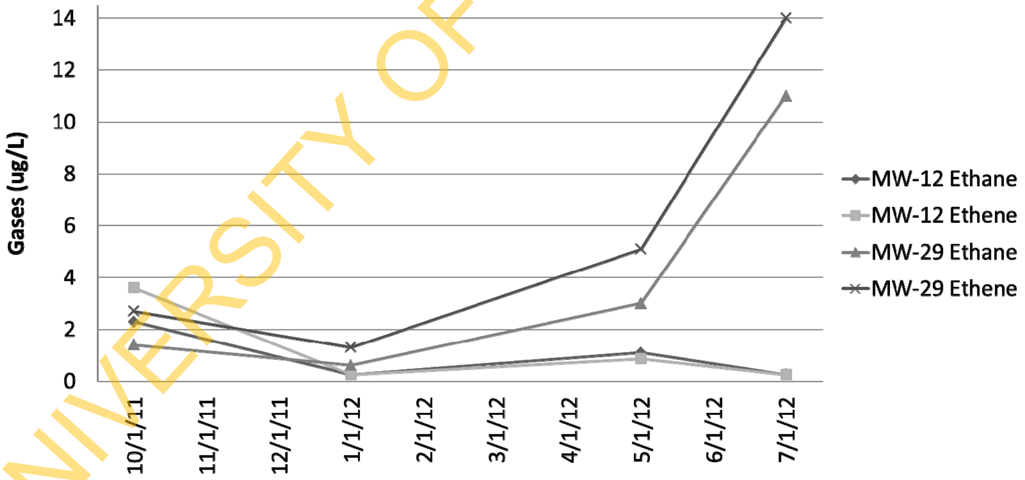

Figure 3. Dissolved Gas Concentrations over Time in the Pilot Test

CONCLUSIONS

The results of the pilot study showed that in situ enhanced biodegradation was an effective technology for 1,1,1-TCA treatment in the groundwater. This technology was recommended for full scale implementation at the pilot study doses. Higher doses of nutrients were also recommended.

FROM BIOAVAILABILITY SCIENCE TO REGULATION OF ORGANIC CHEMICALS

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For over 30 years, investigations into the bioavailability of organic chemicals have been an important focus on a significant amount of research directed at understanding the behaviour of organic pollutants in soils and sediments. Despite this, there is still an apparent lack of understanding and acceptance within environmental regulatory and industrial sectors. However, regulators are now starting to consider bioavailability within risk assessment frameworks for soils and sediments contaminated with organic pollutants. By doing this, more realistic risk assessment and management is possible, rather than using total extractable pollutant concentrations. However, inclusion of bioavailability measurement within risk assessment strategies has been and remains problematic because the lack of standardised methods and statuatory guidelines has hampered the application of bioavailability into the RA and management of contaminated systems.

This presentation will also consider the important of non-extractrable residues (NERs) within risk assessment and management of contaminated land. There have been a number of studies investigating the formation of NERs in soil. Clearly, it is undesirable to be releasing chemicals into the environment, which are known to form significant levels of NERs. Indeed, the formation of NERs has been and continues to be measured in the testing of new pesticides, prior to regulatory approval. Many studies have investigated the mobility and bioavailability of NERs of pesticides, PAHs and PCBs, with the majority of studies having reported little or no measurable extractability, uptake or toxicity in soil.

More recently, a number of researchers have investigated how the formation of NERs could be used as a remediation strategy for contaminated land, by reducing the mobility and bioavailability and therby reducing the risk associated with the target pollutants. For example, black carbon (biochar, activated charcoal, etc) are known to strongly sorb organic chemicals, particularly those considered to be hydrophobic (e.g. PAHs, PCBS, organochlorine pesticides). Many studies have shown that the addition of black carbon to contaminated soil can lead to the formation of residues that are no longer/minimally extractable and considerably less bioavailable than in soils that have not received black carbon amendments.

There are many instances where soils and sediments may be polluted with chemicals that are persistent, due to their low volatility, hydrophobicity and resistance to microbial degradation. This makes these pollutants difficult to remove from the soil technologically and/or economically. Although the formation of NERs means that the pollutants themselves may not be removed from the soil, by actively reducing mobility and bioavailability of the chemicals, the hazards posed by the contamination may be reduced such that the risks to humans, ecological receptors or waters are either removed completely or considered acceptable. However, what is less well known is how permanent NERs are in the environment and what the likelihood of remobilization of the target chemicals may be in the future.

Ultimately, this presentation will propose a framework in which the inclusion of bioavailability measurement(s) may be adopted. This new proposal will provide an opportunity for the inclusion of more detailed interrogative assessment procedure in which bioavailability plays a role, potentially leading to a more pragmatic and realisticrisk assessment. The proposed system is simple and is limited to measuring the totally extractable pollutant, as well as the bioavailable concentration. Under normal circumstances, NERs would not be considered within this proposed RA framework because the risk comes from the extractable fractions in the soils and sediments. Measurement of bioavailability would mean the application of validated and preferably standardised chemical and biological methods and the authors believe that the knowledge already provided by science supports this simplification.

MA32

COMPARISON OF ORAL BIOAVAILABILITY OF BENZO[A]PYRENE IN SOILS USING RODENT AND SWINE MODEL

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INTRODUCTION

Benzo[a]pyrene (B[a]P) is a probable human carcinogen that is ubiquitous in the environment. The current soil guideline value for B[a]P was established using a rodent model in which bioavailability was not considered. Recently, there is a growing acceptance for using swine model for human risk assessment due to the similarity to human in size, physiology and genetics. However, swine is more difficult to handle experimentally and more cost-consuming. Therefore, a comparative study linking bioavailability and swine models could be very helpful in reviewing data from previous rodent studies and validating interspecies extrapolation from rodent to human, via swine. In this study, B[a]P bioavailability expressed as relative bioavailability (RB) was compared between a rodent (rat) and a swine model.

METHODS

Eight soils varying widely in physiochemical properties (Table 1) spiked at 50 mg/kg B[a]P were dosed to adult male Sprague-Dawley rats and swine after 90 days ageing. Following oral dosing, a series of blood samples were taken at different intervals through a tail vein catheter (rats) or from a jugular vein catheter (swine) and the area under the plasma B[a]P concentration-time curve (AUC) was calculated for obtaining bioavailability. A reference material (freshly spiked silica sand) was used in both animal models, at or below the equivalent dose that given in aged soils to establish a dose-response relationship in each model.

Table 1. Key soil properties

Soil ID	TOC (%)	pH	EC (µS cm^{-1})	FPAC[1] (%)	< 6nm pore size proportion (%)
MTA	7.5	5.1	87	5.1	22.7
BDA	3.27	6	75.5	14.4	21.1
N	1.71	7.1	402	7.3	48.8
I	5.06	5.1	69.1	6.3	24.7
GTA	2.88	6.3	143.8	17.6	28.9
TXA	0.96	6.2	36.9	20.1	37.9
GIA	0.78	5.9	53.6	27.9	44.2
GIB	0.72	7.8	192	48.3	47.1

[1]Fine Particle Associated Carbon, defined as (silt (%) + clay (%))/TOC (%) in Duan (2014)

RB of B[a]P after ageing from both rat and swine models were calculated using the following equation:

$$\mathrm{RB} = \frac{\mathrm{AUC_{soil}}/\mathrm{dose_{soil}}}{\mathrm{AUC_{sand}}/\mathrm{dose_{sand}}}$$

RESULTS AND DISCUSSION

In both rat and swine models, linear dose-response relationship have been verified within the study dose range, although the slope of the dose-response curve was different (Figure 1). The slope coefficient for rodent model was at least three times greater than that for the swine model which suggests a far greater response in the smaller animal.

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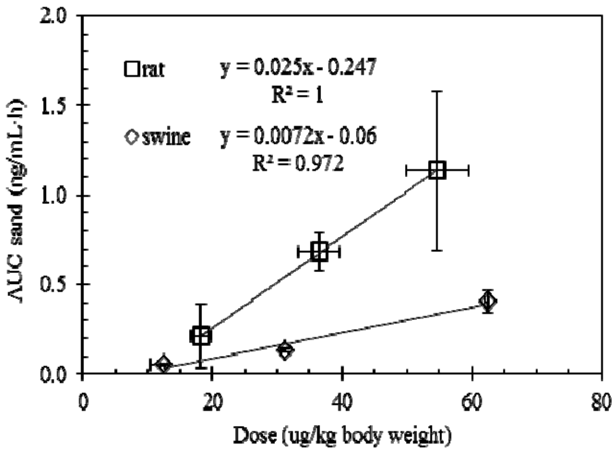

Fig. 1. Dose-response relationship in rat and swine models

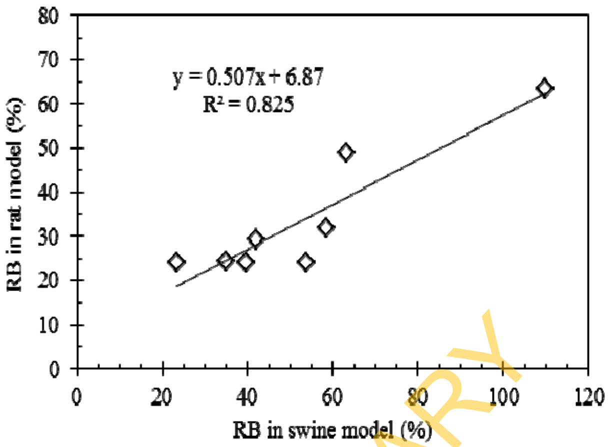

Fig. 2. Correlation between RB in rat and swine models

Relationship of RB in aged soils between swine and rodent models

a) There was a significant relationship between RB determined by swine and rodent model;
b) RB swine was nearly twice that of RB rodent for aged soils.

Soil properties influence RB

When two soils (N and GIB) with elevated pH and EC were excluded from the regression, RB decreased with

(a) an increase in fine particle associated carbon (FPAC) (Fig 3, a); and
(b) an increase in mesopores <6nm (Figure 3, b).

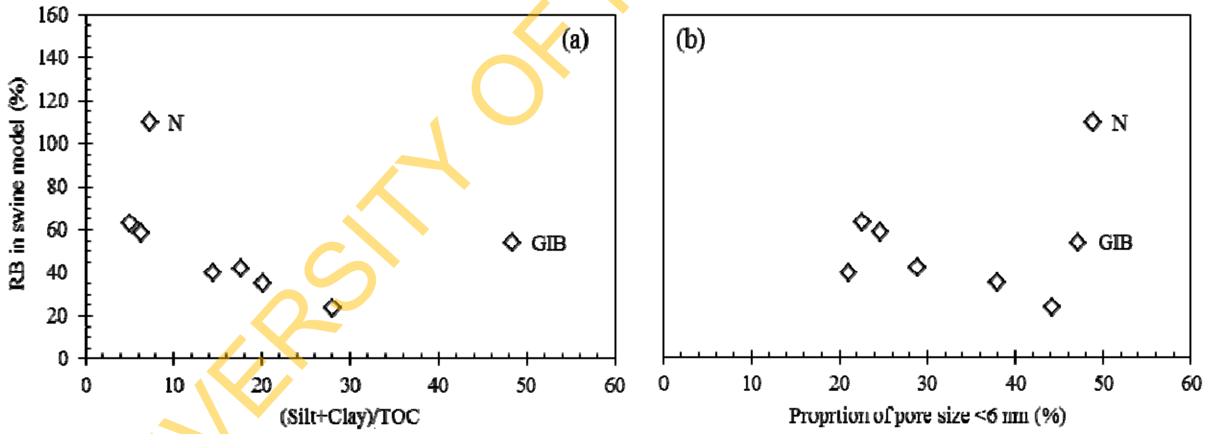

Fig. 3. Correlation between RB in swine and complex soil properties

CONCLUSIONS

Linear dose-response correlations were found in both rat and swine models in the study. Significant (*P* <0.001) correlation exists between RB determined using the two models. The slope of the correlation suggests RB from rat model would be about half of that from swine model. RB was negatively correlated with FPAC and <6nm pore size proportion while pH and/or EC may also influenced it.

REFERENCES

Duan, L., T. Palanisami, Y. Liu, Z. Dong, M. Mallavarapu, T. Kuchel, K. T. Semple and R. Naidu (2014). Effects of ageing and soil properties on the oral bioavailability of benzo[a]pyrene using a swine model. Environ Int 70(0): 192-202.

ENHANCING THE IMMOBILISATION OF LEAD BY PHOSPHATE USING A BIODEGRADABLE CHELATE

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INTRODUCTION

Pb in contaminated soil may not be readily converted to pyromorphite (Moseley et al. 2008) Shooting range soils in particular contain forms of Pb that are relatively bioavailable (Bannon et al. 2009). Reducing bioavailable Pb is desirable for application of chemical stabilisation for remediation, as bioavailable Pb is now used as an endpoint in contaminated site assessment guidelines such as National Environmental Protection Measure (Assessment of Site Contamination) 1999.

Chelating agents have been applied to soils to extract contaminants in soil washing or phytoextraction applications. The ability of chelates to complex metals in the soil may be able to be used to enhance the conversion of Pb to pyromorphite, if the Pb can be displaced from the complex by lowering of the soil pH or displacement by Fe^{3+}. This was examined in four different shooting range soils using the chelate EDDS, which is biodegradable limiting residual effects in the soil (Tandy et al. 2006).

METHODS

Four shooting range soils with differing physicochemical properties and levels of Pb contamination were sieved to 425µm to remove larger metallic bullet fragments. Soil properties were determined using routine methods. Soils were treated in triplicate with EDDS at 4:1 chelate to Pb ratio and incubated at field capacity soil moisture and room temperature for 24 hours prior to application of 2% (by soil weight) Monocalcium phosphate. Another lot of soils had Fe^{3+} ions added in the form of FeCl at a rate of 1% soil weight and incubated for 24 hours after the addition of EDDS and prior to phosphate addition.

Stabilisation with phosphate was assessed after 7 days using an in vitro gastric extraction procedure based on Ryan et al. (2004). Briefly, 1g of <250µm dry soil extracted with 100ml gastric solution (0.4M glycine, pH 2.5 at 37°C) in 125ml Nalgene bottles in a temperature controlled room for 1 hour. Water extractable (WE) Pb was also measured to see the effect of chelate and phosphate addition on this fraction.

RESULTS AND DISCUSSION

EDDS extracted between 40-100% of Pb in the shooting range soils. The result of subsequent stabilisation varied between soils (Figure 1). Bioaccessible Pb was reduced by 24% and 50% compared to phosphate only treatment in soil TV and DA respectively. Bioaccessible Pb increased in the other two soils as a result of EDDS addition before phosphate treatment.

Water extractable Pb increased to varying degrees as a result of the use of EDDS (Table 1). The increase was substantial in MB, likely due the soil pH and the stability of EDDS in the 7-9 range. In DA soil the addition of lime reduced WE Pb and bioaccessible Pb was lower than P only treatment proving perhaps the best treatment option.

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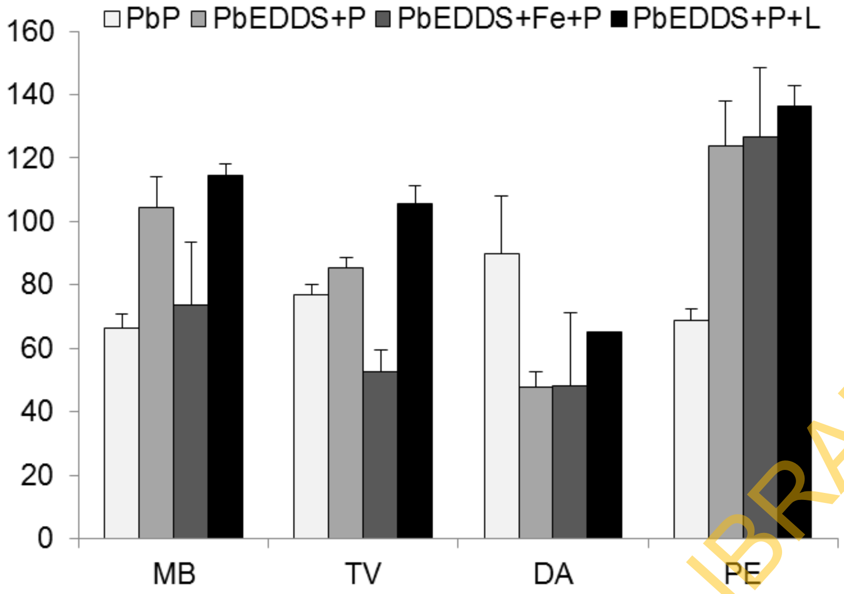

Fig. 1. % Bioaccessible Pb relative to control for treated shooting range soils.

Table 1. Water Extractable Pb (mg/l) in treated shooting range soils

Treatment	MB	TV	DA	PE
Control	107.76	11.9	5.86	1.49
EDDS	2651	279.6	77.8	402.49
EDDS+P	2127	27.16	24.12	27.72
EDDS+Fe+P	2650	24.88	72.78	58.9
EDDS+P+L	589.2	1.3	0.422	0.03

CONCLUSIONS

The use of EDDS and subsequent phosphate treatment resulted in improved stabilisation of Pb in two of the soils. The addition of lime was required to manage WE Pb as a result of the use of EDDS, though lime negatively affected bioaccessible Pb in three of the soils. Additional treatability studies are needed to test amendments that could manage the water extractable portion of Pb.

REFERENCES

Bannon, D.I., Drexler, J.W., Fent, G.M., Casteel, S.W., Hunter, P.J., Brattin, W.J., Major, M.a., 2009. Evaluation of Small Arms Range Soils for Metal Contamination and Lead Bioavailability. Environmental Science & Technology 43, 9071-9076.

Moseley, R.A., Barnett, M.O., Stewart, M.A., Mehlhorn, T.L., Jardine, P.M., Ginder-Vogel, M., Fendorf, S., 2008. Decreasing Lead Bioaccessibility in Industrial and Firing Range Soils with Phosphate-Based Amendments. J Environ Qual 37, 2116-2124.

Ryan, J.A., Scheckel, K.G., Berti, W.R., Brown, S.L., Casteel, S.W., Chaney, R.L., Hallfrisch, J., Doolan, M., Grevatt, P., Maddaloni, M., 2004. Peer reviewed: reducing children's risk from lead in soil. Environmental science & technology 38, 18A-24A.

Tandy, S., Ammann, A., Schulin, R., Nowack, B., (2006) Biodegradation and speciation of residual SS-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing. Environmental Pollution 142, 191-199.

INFLUENCE OF SOIL AGEING ON LEAD BIOAVAILABILITY

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INTRODUCTION

Lead (Pb) is a soil pollutant that has no known essential biological function. Nonetheless it poses a threat to soil-dwelling organisms and human health. Anthropogenic sources of Pb, such as old paints, mining and smelting, have caused Pb contamination of soil in residential areas (Laidlaw and Taylor, 2010;Oyarzun, Lillo et al., 2011). It is well established that the total Pb concentration in soil does not accurately represent its bioavailability (Drexler and Brattin, 2007;Lamb, Ming et al., 2009) and a wide range of chemical and biological techniques are being used to assess the bioavailable fraction in soils (Naidu, Rogers et al., 2003;Naidu, Semple et al., 2008).

Considerable change in metal bioavailability occurs due to a time-dependent process called “ageing” (Naidu, Rogers et al., 2003;Vig, Megharaj et al., 2003). Ageing causes metal bioavailability to decrease with time. Monitored natural attenuation (MNA) of contaminated soils has served as an attractive remediation option for decades. In addition to natural attenuation processes, one assumption in MNA is that contaminant bioavailability in soils decrease with time (i.e. with ageing) (Naidu, Megharaj et al., 2000).

The current study investigated the extent and intensity of the changes in Pb bioavailability in four contrasting soils over a time period (56 days) until the Pb relative bioavailability (RB) levels achieved a steady state. This helped to assess the extent of: firstly, bioavailability change in each soil; and secondly, correlation of these changes with the soil properties.

METHODS

Four soils used in this study were collected from uncontaminated sites in Queensland and South Australia. Relative bioavailability of soils spiked with 1500 mg Pb/kg were measured in swine that were fed these soils, throughout an ageing period (56 days) to investigate relationships between soil properties and *in vivo* bioavailability of Pb. Spiked soils were used to minimize the effect of varying sources of Pb on RB.

Metal sorption studies were conducted by equilibrating 1-g samples of soil in separate tubes with varying concentrations of Pb acetate in 30 ml 0.03 mol/L $NaNO_3$, in duplicate.

In this study K_d was obtained from the Freundlich adsorption equation.

In total 78 Landrace-large white female swine weighing 20-25 kg were used for the bioavailability assays. The pigs were given a dose (oral or IV) of Pb either as a solution of soluble Pb salt [Pb acetate = $(CH_3COO)_2Pb.3H_2O$] or soil contaminated with the same source of Pb. Blood samples were collected at 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 24, 48, 96 and 120 h following dose administration. These samples were then immediately diluted 20-fold in diluent solution containing 1- butanol (2% w/v), EDTA (0.05% w/v), Triton X-100 (0.05% w/v) and ammonium hydroxide (1% w/v) in Milli-Q water, and stored at 2-8 °C prior to Pb analysis. Bioavailability was derived from the areas under the blood Pb concentration – time curves (AUC) described by a two-compartment pharmacokinetic model (Zhang, Huo et al., 2010) for results from Pb administered as IV (intravenous) dose, oral solution or as spiked soils.

RESULTS AND DISCUSSION

The bioavailability of Pb in soils in the freshly spiked soils highlighted a significant inverse correlation with pH (r=-0.909, p<0.05) and EC (R=-0.918, P<0.05) which indicated that an increase in pH or EC led to a significant decrease in RB. Many researchers have shown increased metal sorption occurring with increasing pH due to an increase in surface negative charge of the constant potential soil constitutes leading to increased sorption and as a consequence low Pb or metal bioavailability (Cao, Ma et al., 2011;Naidu, Bolan et al., 1994). In contrast to freshly spiked soil where Pb RB showed a significant correlation with pH and EC, the steady state RB of soils significantly (p<0.05) correlated with clay content (r=-0.95) and CEC (r=-0.91),

The RB of Pb in GTA, IWA and MLA decreased from their initial Pb RB values until a steady state RB of 34%, 45% and 59% was reached respectively by the 56th day. In contrast, however, to these RB decreases, NTA soil indicated no change in RB over the whole ageing period of the experiment. The lack of change in RB in the NTA soil over time was attributed to it achieving a steady state RB within a very short time due to its comparatively high sorptive capacity (kd=112).

REFERENCES

Cao, X., et al. (2011). Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. Environmental Science & Technology 45(11), 4884-4889.

Drexler, J. W. and W. J. Brattin (2007). An in vitro procedure for estimation of lead relative bioavailability: with validation. Human and Ecological Risk Assessment: An International Journal 13(2), 383 - 401.

Laidlaw, M. A. S. and M. P. Taylor (2010). Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. Environmental Pollution 159, 1-9.

Lamb, D. T., et al. (2009). Heavy metal (Cu, Zn, Cd and Pb) partitioning and bioaccessibility in uncontaminated and long-term contaminated soils. Journal of Hazardous Materials 171(1-3), 1150-1158.

Naidu, R., et al. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. European Journal of Soil Science 45(4), 419-429.

Naidu, R., et al. (2000). Bioavailability, definition and analytical techniques for assessment and remediation of contaminated (inorganic and organic) soils. Contaminated site remediation: From Source Zones to Ecosystems. Proceedings of the 2000 Contaminated Site Remediation Conference, Melbourne, Australia, DTIC Document.

Naidu, R., et al. (2003). Bioavailability of metals in the soil plant environment and its potential role in risk assessment. Bioavailability, toxicity and risk relationships in ecosystems. 4th International Symposium on the Biogeochemistry of Trace Elements, Berkeley, California, USA, 23-26 June 1997., Science Publishers, Inc.

Naidu, R., et al. (2008). Bioavailability - new concepts and definitions. Developments in soil science. Elsevier. 7-7.

Oyarzun, R., et al. (2011). The Mazarrón Pb–(Ag)–Zn mining district (SE Spain) as a source of heavy metal contamination in a semiarid realm: Geochemical data from mine wastes, soils, and stream sediments. Journal of Geochemical Exploration 109(1–3), 113-124.

Vig, K., et al. (2003). Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review. Advances in Environmental Research 8(1), 121-135.

Zhang, Y., et al. (2010). PKSolver: An add-in program for pharmacokinetic and pharmacodynamic data analysis in Microsoft Excel. Computer Methods and Programs in Biomedicine 99(3), 306-314.

REACHING A CONSENSUS ON BIOAVAILABILITY MEASUREMENTS: A CASE STUDY OF Pb IN DUTCH TOWN SOILS

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INTRODUCTION

Measuring the bioavailability of potentially harmful elements has received much attention in the current literature with particular interest in Pb (Zia et al., 2011). Measuring techniques can take the form of in-vivo studies using humans or animals, in-vitro tests which mimic the gastro-intestinal tract and use bioaccessibility as a conservative analogue of bioavailability and geochemical tests which look at the chemical form Pb in the soil and use the relative lability of the different chemical forms of Pb to estimate bioaccessibility/bioavailability. In this study the bioavailability of Pb in soils from seven Dutch towns has been estimated using all three approaches. The comparison between all results provides some insights into the mechanisms controlling Pb bioaccessibility in the urban environments of old Dutch towns.

METHODS

Soil sampling

Soil samples from the towns of Leiden, Utrecht, Rotterdam, Maastricht, De Ryp, the Haigh and Nymegen. The soil sampling and sample preparation has been previously described (Van Kesteren et al., 2014)

In-vivo Bioavailability Testing

The bioavailability of Pb in the soils was determined using a study conducted on juvenile swine and has been previously described (Van Kesteren et al., 2014).

In-vitro Bioaccessibility Testing

Assessment of the bioaccessible Pb was undertaken using the Unified Barge Method (UBM) (Denys et al., 2009), a gastro-intestinal sequential extraction at physiologically relevant pHs, temperature and timescales to emulate fasting conditions (to provide a conservative estimation) in the human gut.

Sequential extraction test

The Chemometric Identification of Substrates and Element Distributions (CISED) method was used to measure the fractionation of Pb in the soils (Cave et al., 2015) The soils were leached as follows: approximately 1 g of sample was accurately weighed into 30 ml Oakridge centrifuge tubes and 10 ml of the starting leachant (de-ionised water) was added. The suspensions were rotated on an end-over-end shaker for 10 minutes then centrifuged for five minutes at 4350 rpm. The supernatant was collected for analysis by ICP-AES, before the next leachant was added and the process was repeated. Seven leachate solutions (ranging from deionised water through to 5M aqua-regia) repeated three times each were used giving 21 extracts per sample. The data from the each set of 21 extracts for each soil was subjected to a self-modelling mixture algorithm which identifies the main acid soluble geochemical components in the soil and fractionation of the target elements between them (Cave, 2009).

RESULTS AND DISCUSSION

The CISED extraction identified between 8 and 13 distinct geochemical components in the soils. Fig.1 shows the elemental composition of the geochemical component in each soil which contains the largest proportion of Pb. For Leiden, Utrecht, Rotterdam, DeRuyp and The Haigh these components have a common theme of three elements namely Pb, Al and P. For each of these towns there is good agreement between the in-vivo bioavailability and the UBM bioaccessibility and the Pb containing component contains > 65 % of the total Pb. For Maastricht the main Pb bearing fraction is dominantly Al and Si and the UBM bioaccessibility gives a low value compared to the in-vivo study.

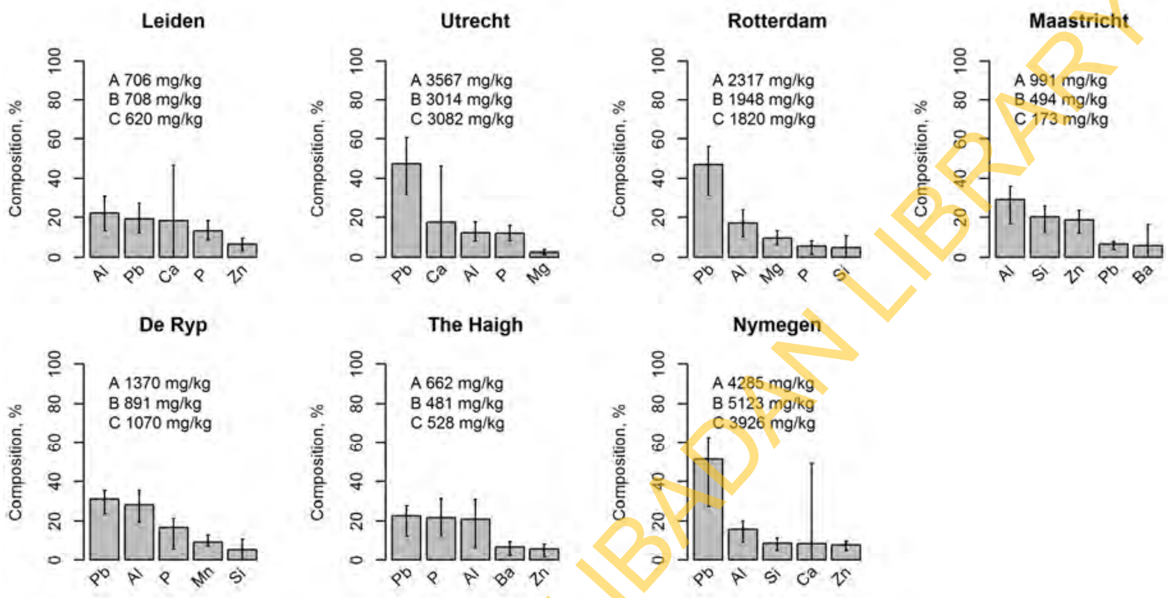

Fig. 1. Composition of the 5 most abundant elements in the main Pb containing fractions for each town soil. A is the total Pb content by XRF; B is the Pb content of the main Pb containing fraction; and C is the UBM bioaccessible Pb.

CONCLUSIONS

The Pb/Al/P fraction suggest the Pb in these soils may be in the form of plumbogummite ($PbAl_3(PO_4)_2(OH)_5\cdot H_2O$) which has been shown to be present in soils e.g. (Adams et al., 1973). It appears that this Pb fraction is bioavailable as shown by the in-vivo and in-vitro results. The Pb in the aluminosilicate phase in Maastricht is far less bioavailable and there is poorer agreement between in-vivo and in-vitro results (Van Kesteren et al., 2014).

REFERENCES

Adams, J A, Howarth, D T, and Campbell, A S. 1973. Plumbogummite minerals in a strongly weathered new zealand soil. *Journal of Soil Science*, Vol. 24, 224-231.

Cave, M, Wragg, J, Gowing, C, and Gardner, A. 2015. Measuring the solid-phase fractionation of lead in urban and rural soils using a combination of geochemical survey data and chemical extractions. *Environmental Geochemistry and Health*, accepted

Cave, M R. 2009. The use of self modelling mixture resolution for the interpretation of geochemical data. *British Geological Survey*, IR/08/035.

Denys, S, Caboche, J, Feidt, C, Hazebrouck, B, Dor, F, Dabin, C, Floch-Barneaud, A, and Tack, K. 2009. Oral bioavailability and bioaccessibility in humans of metals and metalloids from polluted soils: Definitions, measure protocols and international operational feedback. *Environnement Risques & Sante*, Vol. 8, 433-438.

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MA42

QUANTIFYING STATISTICAL RELATIONS BETWEEN COMMONLY USED *IN VITRO* MODELS FOR ESTIMATING LEAD BIOACCESSIBILITY

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INTRODUCTION

Exposure to lead (Pb) is a global concern due to its widespread occurrence and adverse health effects. It has been well established that lead exposure affects the development of neuronal systems, impacts on cell function and reduces the intelligence quotient in children (Shannon, 1998). In terms of relevant pathways, contaminated soil poses a significant risk due to children's hand-to-mouth behavior and higher metabolic rate (U.S. Environmental Protection Agency, 2007). In recent decades *in vitro* methods have been developed and proved to be fast, economic, reliable, and reproducible for estimating Pb bioaccessibility (BAc). Currently, various *in vitro* methods are developed to determine the Pb BAc. Although differences among the *in vitro* models have been discussed in the previous studies, to our best knowledge, no statistical relations among the five *in vitro* models have been quantified.

In this study, the Pb BAc values of 10 contaminated soils were determined using RBALP, UBM, SBRC, RIVM, and PBET models. The impacts from the in vitro procedures, such as mixing mode, solid:liquid (S:L) ratio, were also addressed. Moreover, data from previous published studies were included in my regressions study. This study provided a scientific basis to minimize uncertainties for measurement of lead BAc in human health risk assessment.

METHODS

Ten Pb contaminated soils were collected from mining areas in Australia. All samples were air-dried in ambient conditions ($< 37^{o}$C), and sieved using a 250 µm stainless steels sieve. Lead bioaccessibility was determined by the RBALP, UBM, SBRC, RIVM, and PBET models, detailed description please refer to previous study (Juhasz et al., 2013, Hettiarachchi et al., 2003, Oomen et al., 2006). All the statistical analyses of the data were performed using the Statistical Package for the Social Sciences (SPSS).

RESULTS AND DISCUSSION

The mean value of Pb BAc for the SBRC, PBET, UBM, RIVM (0.6) and RIVM (0.06) models are 54.5%, 16.2%, 50.2%, 58.1% and 72.3%, respectively, particularly the BAc based on PBET was significantly lower than the others. No relationships between the soil properties and lead BAc were observed in this study. However, several factors were observed that influences the measured BAc: 1) relatively higher BAc were found using mixing mode of the end-over-end rotation than that of the shaking for the RBALP, SBRC and PBET; 2) S:L ratio limits the extraction ability of the UBM and RIVM models; 3) high pH probably reduce the measured BAc as demonstrated across the *in vitro* models.

In this study, the RBALP model has been selected as the reference variable (dependent variable (y)) to address the correlations among *in vitro* methods as plotted in Figure 1. Due to the limitation of UBM and RIVM (0.6), sample Nos. 5 and 7 are considered to be outliers when establishing relations. Significant correlations of Pb BAc for gastric phase were found between RBALP and SBRC (a), RBALP and RIVM (0.06) (b), RBALP and UBM (c), and RBALP and RIVM (0.6), while no significant correlation was found between PBET and RBALP.

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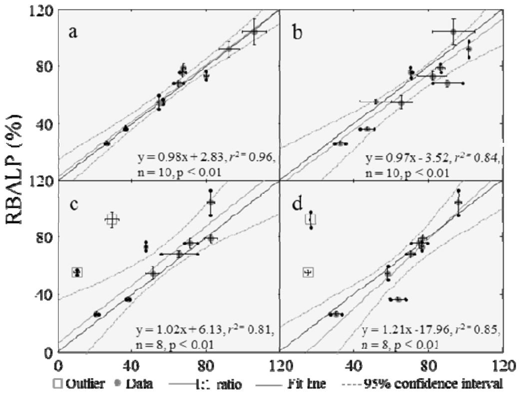
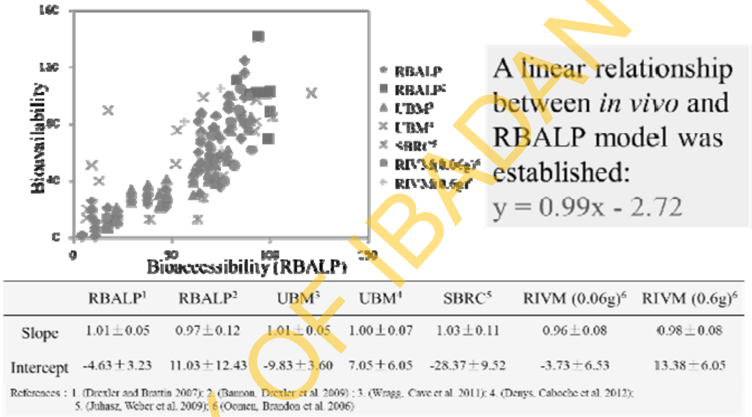


a. SBRC (G-phase) & RBALP; b. RIVM (0.06) (G-phase) & RBALP;
c. UBM (G-phase) & RBALP; d. RIVM (0.6) (G-phase) & RBALP;

Figure 1. Correlations of G-phase for four *in vitro* models in the present study.

Previous published data were applied in current established relations, and a linear relationship between Pb bioavailability and the RBALP model was established (as shown in Figure 2). For these previous studies, the slopes of the relationship after transfer ranged from 0.96 to 1.01.



A linear relationship between *in vivo* and RBALP model was established:
y = 0.99x - 2.72

	RBALP[1]	RBALP[2]	UBM[3]	UBM[4]	SBRC[5]	RIVM (0.06g)[6]	RIVM (0.6g)[6]
Slope	1.01±0.05	0.97±0.12	1.01±0.05	1.00±0.07	1.03±0.11	0.96±0.08	0.98±0.08
Intercept	-4.63±3.23	11.03±12.43	-9.83±3.60	7.05±6.05	-28.37±9.52	-3.73±6.53	13.38±6.05

References : 1. (Drexler and Brattin 2007); 2. (Bannon, Drexler et al. 2009) ; 3. (Wragg, Cave et al. 2011); 4. (Denys, Caboche et al. 2012);
5. (Juhasz, Weber et al. 2009); 6 (Oomen, Brandon et al. 2006)

Figure 2. Comparisons of the data from previous studies and the present study.

CONCLUSIONS

Lead bioaccessibility varies depending on the *in vitro* models used. Correlations among the *in vitro* models were quantified and we concluded that the G-phase is reliable to indicate Pb BAc. The end-over-end rotation is an appropriate mode to simulate digestive extraction. Solid:liquid ratio has a significant influence on Pb BAc. The relationships established in our study is reliable and can be used to predict Pb bioavailability.

REFERENCES

Hettiarachchi, G. M., Pierzynski, G. M., Oehme, F. W., Sonmez, O. & Ryan, J. A. 2003. Treatment of contaminated soil with phosphorus and manganese oxide reduces lead absorption by Sprague–Dawley rats. Journal of environmental quality, 32, 1335-1345.

Juhasz, A. L., Smith, E., Weber, J., Rees, M., Kuchel, T., Rofe, A., Sansom, L. & Naidu, R. 2013. Predicting lead relative bioavailability in peri-urban contaminated soils using in vitro bioaccessibility assays. Journal of Environmental Science and Health, Part A, 48, 604-611.

Oomen, A. G., Brandon, E. F. A., Swartjes, F. A. & Sips, A. 2006. How can information on oral bioavailability improve human health risk assessment for lead-contaminated soils? Implementation and scientific basis. Rijksinstituut voor Volksgezondheid en Milieu RIVM.

Shannon, M. 1998. Lead poisoning from an unexpected source in a 4-month-old infant. Environmental health perspectives, 106, 313.

ASSESMENT OF ARSENIC SPECIATION AND BIOACCESSIBILITY IN MINE-IMPACTED MATERIALS

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INTRODUCTION

Operational and legacy gold (Au) mine sites exist throughout the world as a result of current and historical activities. These sites are numerous and are typically associated with elevated concentrations of arsenic (As) due to the association of both As and Au with sulphidic phases. Arsenic contamination at mine sites is a consequence of Au processing which results in three predominant contaminated materials; tailings, calcinated and slime materials. Tailings are typically associated with refuse material, i.e. materials left over after the process of separating the valuable fraction from the uneconomic fraction of an ore. Calcinated materials are waste products resulting from high temperature processes applied to ores that facilitates thermal decomposition, phase transition and the removal of volatile fractions. In contrast, slimes are fine materials, commonly associated with settling tanks and tailings ponds, produced during mechanical crushing that are separated from the valuable ore component. As a consequence of these physical and thermal processes, As speciation, As concentration and other physicochemical properties of the contaminated matrix will vary which may impact on the outcomes of As bioaccessibility testing. However, despite their different properties, 'mine wastes' are often reported under a generic descriptor which may underrepresent As bioaccessibility of individual mine-impacted materials and therefore impact on human health exposure assessment. In this study, mine-impacted materials were categorised and characterised to determine the influence of ore processing on As bioaccessibility.

MATERIALS AND METHODS

Mine-impacted materials ($n = 50$) were collected from Victoria, Australia and categorized into three source materials based on physical appearance; tailings ($n = 35$), calcinated ($n = 10$) and slimes ($n = 5$). Total metal / metalloid concentrations in the < 2 mm and < 250 µm soil particle size fraction was determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) following acid digestion. Arsenic bioaccessibility in mine-impacted materials was determined using the <250 µm soil particle size fraction and the gastric phase of the Solubility Bioaccessibility Research Consortium (SBRC) assay. As speciation was determined using X-ray absorption near-edge structure (XANES).

RESULTS AND DISCUSSION

The concentration of As in these materials varied over several orders of magnitude (30-47,000 mg kg^{-1}), with median concentrations of 500, 10,800 and 1,500 mg kg^{-1} for tailings, calcinated and slimes respectively. Other physicochemical properties varied between the mine-impacted materials notably total (2-110 g kg^{-1}) and amorphous Fe (0.18-14.2 g kg^{-1}) concentrations. When As bioaccessibility was assessed using the SBRC assay, As bioaccessibility was variable, with mean values of 30%, 49% and 82% for tailings, calcinated and slimes respectively. An analysis of variance (ANOVA) determined that As bioaccessibility was significantly different ($P < 0.05$) between source materials presumably due to differences in As speciation, in addition to the concentration of total and amorphous

Fe which may influence As dissolution / precipitation under gastrointestinal conditions. XANES analysis identified arseniosiderite [$Ca_2Fe^{3+}_3(AsO_4)_3O_3 \bullet 3(H_2O)$], yukonite [$Ca_7Fe^{3+}_{11}(AsO_4)_9O_{10} \bullet 24.3(H_2O)$], realgar [AsS], loellingite [$Fe^{2+}As_2$] and mineral sorbed As^V species in mine-impacted materials with more crystalline forms prevalent in tailings and a greater proportion of mineral sorbed As^V present in calcinated materials.

CONCLUSION

In recent years, research into mine-impacted materials has reported considerable variability in As bioaccessibility with a mean value of ~15%. Outcomes from this research highlight that variability in As bioaccessibility can be prescribed to As speciation and matrix physicochemical properties while categorizing samples into tailings, calcinated and slime materials can provide some notional indication of potential exposure.

COPPER DECREASES ARSENIC SOLUBILITY, GROWTH AND UPTAKE AT TOXIC DOSE LEVELS (EC10 AND EC50)

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INTRODUCTION

Widespread contamination of soil with metal(loid)s is a serious concern to environment and human health. Arsenic (As) occurs as a co-contaminant with copper (Cu) in different mining sites, especially in coper smelters, mining sites associated with gold and also in wood preservative sites. The contaminant can influence the original bioavailability and toxic effect of this individual. However, there is no sufficient data regarding mixture studies (De Zwart and Posthuma 2005). Generally, mixture toxicity is measured based on additive approach. As a result, combined toxicity may be over/under estimated that challenges the risk assessment for mixed contaminants. Cu may interact with As to influence toxicity directly within the organism. Alternatively, Cu-As interactions at the solid solution may influence toxicity due to modification of solubility. The aim of this study was to investigate the interaction of binary mixtures of As with Cu in different soil types based on solubility, growth and bioaccumulation on cucumber plant.

METHODS

Soils (5) were collected from different parts of Australia. After air drying and sieving, soils were first spiked with arsenic at 10 different concentrations (2, 4, 8 ··· ·1024 mg/kg) and 2 weeks later, Cu was added in each arsenic spiked soil at 10% and 50% inhibition level based on previous study (Tables -1). After 8 weeks of ageing, pots were prepared. Cucumber (*Cucumis sativa L*) seeds were sown in each pot to ensure sufficient germination (10-12 seeds). After two weeks, seedlings were thinned to 5 plants per pot. Plants were harvested and fresh weight was measured after 4 weeks of growing under greenhouse condition (~16 - 30˚C). After washing and drying, shoots were weighing for dry weight and measured As and Cu content in shoots by acid digestion. Then Pore water was analysed for free Cu (Ion Selective Electrode), soluble total metal(loid)s, pH and dissolved organic carbon(DOC). Data was analysed by sigmoidal dose response model using SPSS and Grapher software. For mixture interactions, a response additive model used to predict mixture toxicity.

Table -1: Sources of soil with their corresponding toxic level for copper on cucumber growth

Soil code	Source	Cu EC50 (mg/kg)	Cu EC10(mg/kg)
BKA	QLD	893	626
MGA	SA	1,698	709
PBA	SA	844	174
TAA	Vic	873	410
YEA	NSW	918	334

RESULTS AND DISCUSSION

Plant growth

Cucumber exhibited differential growth in different soils. Relative growth (13%, average) was observed at 1024 (mg/kg) in TAA soil whereas no growth was observed at 256 (mg/kg) in PBA soil. Plant growth was changed significantly in Cu-As combination (Figure -1).

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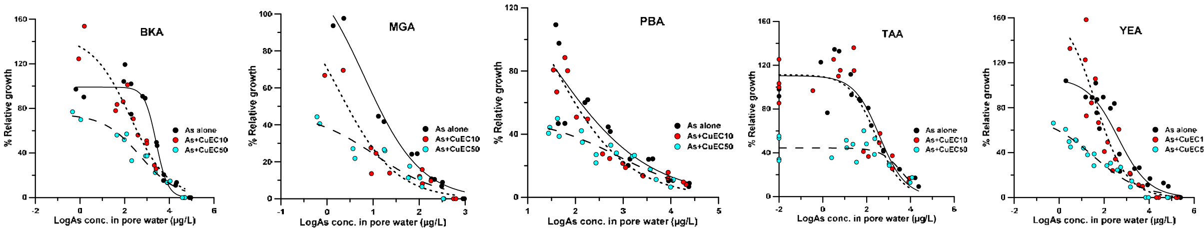

Figure-1: Sigmoidal growth response of cucumber (*Cucumis satva L*) against arsenic pore water concentration on different soils on dry weight basis. The slope of As sigmoidal curves was changed in presence of Cu in every soil. Therefore effective toxic doses (ECx) were also changes. Most of the cases interaction was antagonistic based on response additive model in a broad range of concentration.

Solubility & bioaccumulation

Arsenic concentration was significantly reduced in pore water as well as shoot uptake in presence of copper. The slopes of each curve was similar, however, the intercepts changed significantly (P< 0.05) in each soils (Figure- 2). On the other hand Cu concentration was changed only in PBA and MGA.

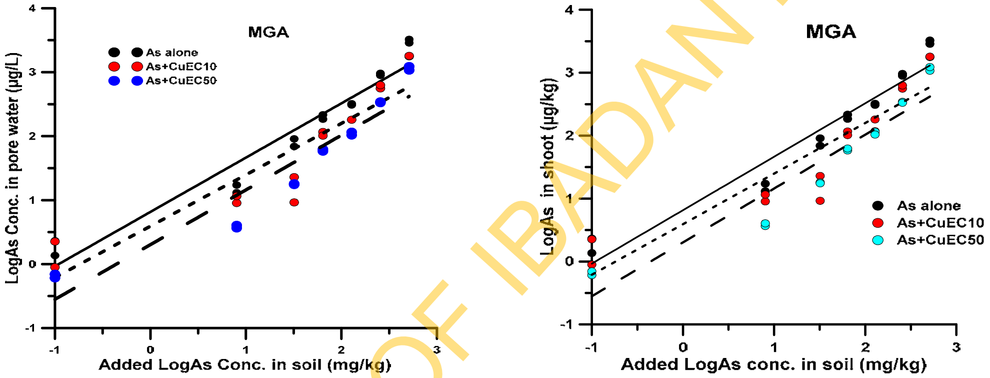

Figure -2: Pore water and shoot uptake concentration against added arsenic in MGA soil.

Equations for MGA pore water

$As_{PW} = -176 + 5.9\ As_{\text{added in soil (As alone)}}$

$As_{PW} = -112 + 3.5\ As_{\text{added in soil (As +CuEC10)}}$ (P<0.05)

$As_{PW} = -75 + 2.3\ As_{\text{added in soil (As +CuEC50)}}$ (P<0.05)

Equations for shoot uptake in MGA soil

$As_{\text{uptake}} = 888 + 17.3\ As_{\text{added in soil (As alone)}}$

$As_{\text{uptake}} = 326 + 22.2\ As_{\text{added in soil(As +CuEC10)}}$ (P<0.05)

$As_{\text{uptake}} = -97 + 15.2\ As_{\text{added in soil(As +CuEC50)}}$ ((P>0.05)

CONCLUSIONS

Cu decreased As concentration in soil environment as well as shoot uptake in cucumber which influenced the overall toxicity.

REFERENCE

De Zwart, D. and L. Posthuma (2005). "Complex mixture toxicity for single and multiple species: proposed methodologies." Environmental Toxicology and Chemistry 24(10): 2665-2676.

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CHLORINATED SOLVENT SITE REMEDIATION: STATE OF THE PRACTICE

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INTRODUCTION

Society has made considerable progress in cleaning up contaminated soil and groundwater. However, it is still extremely difficult to remove enough contaminant mass to achieve typical concentration-based cleanup goals at many sites. This challenge has been particularly difficult for sites with chlorinated solvents in groundwater, with the result that many sites still have not been adequately treated, or have been treated but still require long-term management and monitoring. For example, the US Department of Defense (DoD) has not been able to meet its overall Installation Restoration Program (IRP) goals, with too many sites that have not yet attained “response complete” or closure status. The difficulty meeting the goals is due to the “complex nature of IRP sites ... and the limitations of available technology”, a problem that “is not unique to DoD” (US DoD, 2012).

Much of DoD’s research on this topic is funded by SERDP and the related Environmental Security Technology Certification Program (ESTCP). Since 2000, this SERDP- and ESTCP-funded research has been guided by three workshops that reflect the changing priorities and progress over that time. The first workshop (2001) stressed the need to obtain valid data on the performance and costs of the major source zone remediation technologies. The second (2006) was titled Reducing the Uncertainty in Source Zone Remediation. The most recent (2013) focused on the needs for long term management following active treatment. These needs include both less costly monitoring techniques, and technologies to quantify slow natural and enhanced attenuation processes

This presentation will cover the lessons learned from the earlier work and the objectives and findings of the relevant recent and ongoing projects.

LESSONS LEARNED

Key lessons learned regarding source zone remediation were summarized in Stroo et al. (2012), and include: 1) complete restoration is rare; 2) source “architecture” is critical and often poorly characterized; 3) contaminant diffusion into lower-permeability zones can create a very long-lasting secondary source; 4) high-resolution monitoring and flux measurements can improve remediation and long-term management; and 5) source zones attenuate naturally, often at significant and measurable rates. Data illustrating these lessons will be presented, along with summaries of the status, costs, and performance of all of the major source zone treatment technologies.

RECENT RESEARCH

Most of the relevant recent work falls under three specific Requests for Proposals (RFPs) - Assessment and Optimization of Remediation Technologies, Fine Scale Delineation of Contaminated Subsurface Environments, and Long Term Natural Attenuation. The rationale for these funding decisions is briefly described, along with the projects within each topic.

The need to optimize remediation technologies results from the significant challenges that remain at many sites. Thousands of remedial systems have been installed at DoD sites, but too often the remedial objectives have not been met and the ongoing costs remain unacceptably high. To address these challenges, SERDP sought to identify research and demonstration strategies that could improve remediation success, reduce risk, and ultimately reduce the cost to complete. The projects selected include developing improved diagnostic technologies (such as CSIA and proteomics), optimizing redox-based chemical treatment, and improving reagent delivery by using shear-thinning fluids.

Research on fine scale delineation is driven by the need for more accurate conceptual site models, which would help to better target remedial actions and to quantify relatively slow attenuation processes. The practical limitations on our ability to delineate the contaminant distribution and define the biogeochemical conditions in the subsurface clearly limit our ability to remediate many sites cost-effectively. However, there is also some concern regarding the actual benefits of more costly characterization techniques. The projects under this topic include the use of innovative geophysical tools in fractured media and the development of high-resolution passive monitoring devices.

Finally, several natural attenuation processes can impact the mobility and/or the transformation of contaminants in the subsurface, and these processes may provide adequate protection after source control. However, some of these processes may operate slowly, or may impact only a portion of the impacted subsurface. A greater understanding of the spatial extent and rates of these natural attenuation processes is therefore needed. In particular, a better understanding of the fluxes from less mobile regions and the degradation near and within those regions would be helpful. The projects arising from this SON will be described briefly.

REFERENCES AND RESOURCES

Kueper BK, HF Stroo, C Vogel, CH Ward (Editors). 2014. Chlorinated Solvent Source Zone Remediation. Springer, New York, NY. 716 p.

Leeson A, HF Stroo, and PC Johnson. 2013. Groundwater remediation today and challenges and opportunities for the future. Groundwater 51(2):175-179.

National Research Council (NRC). 2013. Alternatives for Managing the Nation’s Complex Cotnaminated Groundwater Sites. National Academies Press, Washington, DC. 284 p.

Stroo HF, M Unger, CH Ward, MC Kavanaugh, C Vogel, A Leeson, JA Marqusee, B Smith. 2003. Remediating chlorinated solvent source zones. Environmental Science & Technology 37:224A–230A.

Stroo HF, A Leeson, JA Marqusee, PC Johnson, CH Ward, MC Kavanaugh, TC Sale, CJ Newell, KD Pennell, CA Lebrón, and M Unger. 2012. Chlorinated ethene source remediation: Lessons learned. Environmental Science & Technology 46:6438−6447. Available at: pubs.acs.org/doi/full/10.1021/es204714w.

Stroo HF, CH Ward (Editors). 2010. *In Situ* Remediation of Chlorinated Solvent Plumes. Springer. New York, NY. 786 p.

SERDP 2001, 2004, and 2013 Workshop Reports. Available at: http://serdp.org/News-and-Events/Conferences-Workshops/Past-ER-Workshops.

United States Department of Defense (US DoD). 2012. Annual Report to Congress (Fiscal Year 2012). Reports (1995-2012) available at: http://www.denix.osd.mil/arc.

VARIABILITY AND UNCERTAINTY ASSOCIATED WITH SAMPLING, ANALYSIS, AND RISK ASSESSMENT

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INTRODUCTION

Variability associated with sampling and analysis of environmental media and the uncertainty and bias inherent in risk assessment can impact the site conceptual model and thereby influence the final remedy selection and engineering design.

The intrinsic variability in soil concentrations across short distances (even a few centimeters) and the temporal and spatial variability in groundwater can be challenging when determining the extent of contamination.

ANALYTICAL VARIABILITY

Sampling variability and bias can be compounded by analytical variability associated with sample preparation techniques, analyst competencies, and instrument capabilities that can influence the final reported results. An example will be provided to demonstrate that sample preparation techniques and analyst competencies are critical to identifying and quantifying the compound being analyzed.

BIAS & UNCERTAINTY IN RISK ASSESSMENT

Data generated from this inexact process is then utilized in risk assessment calculations that bring additional uncertainty and bias. This is attributable to risk assessment's use of toxicity values developed by extrapolating from animal studies to human toxicity and from high-to-low-doses. Uncertainty is compounded by its inability to address possible synergistic or antagonistic effects associated with multiple chemical exposures.

The outcome of this cumulative variability and/or uncertainty may lead to misestimates of the actual risk and improper remedy selection and cleanup activities.

CONCLUSIONS

While this uncertainty can never be eliminated completely, the purpose of this presentation is to shed some light on the sources of variability and their relative importance, and to present ways the cleanup team can manage this uncertainty to allow the team to properly manage the ambiguity associated with the risk assessment process.

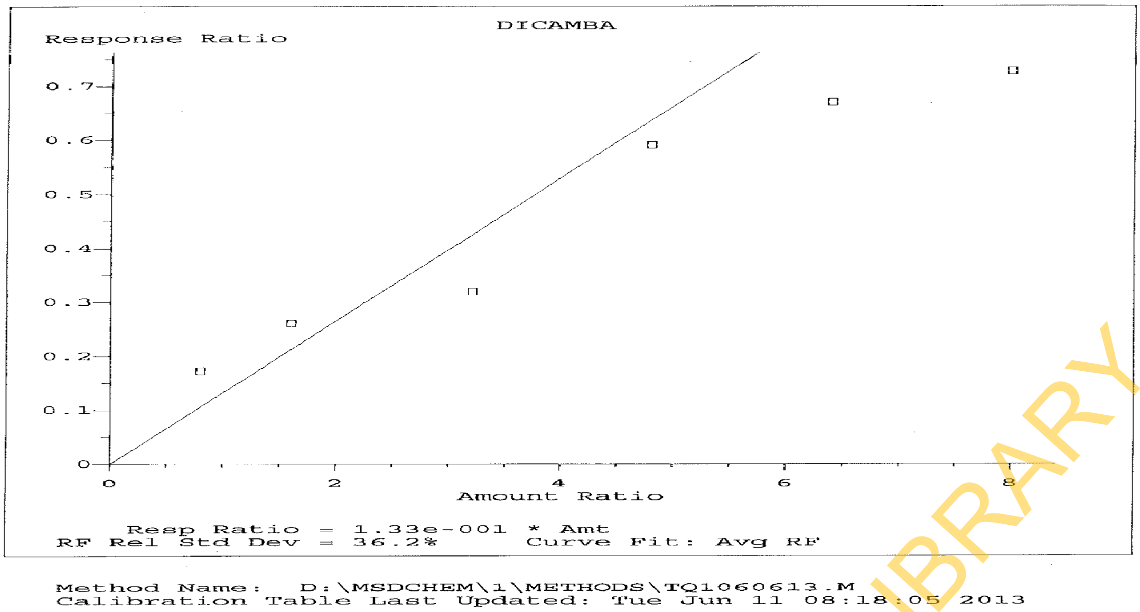
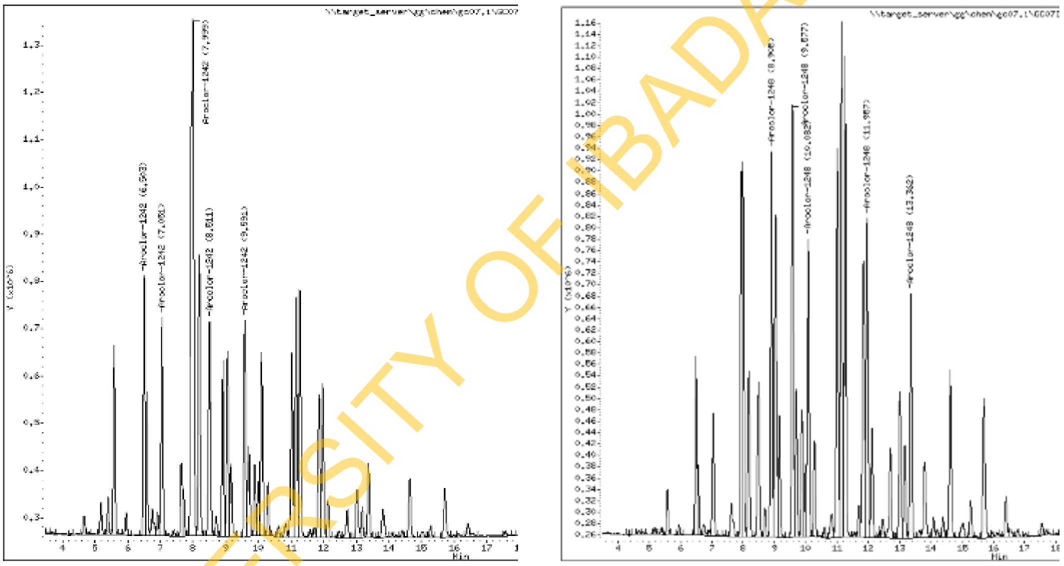


Fig. 1 Typical Calibration Curve



Aroclor-1242

Aroclor-1248

Fig. 2 Typical chromatograms for Aroclor-1242 and Aroclor-1248

REFERENCES AND RESOURCES

The ITRC - Decision Making at Contaminated Sites: Issues and Options in Human Health Risk Assessment
(RISK-3) Jan-15

Factors Influencing Variability in Groundwater Monitoring Data Sets
by T.E. McHugh, L.M. Beckley, C.Y. Liu, and C.J. Newell

CHARACTERIZATION OF CONTAMINANT DISTRIBUTION TO MEET SITE-SPECIFIC REMEDIAL OBJECTIVES AT SPATIAL RESOLUTIONS APPROPRIATE TO SUBSURFACE CONDITIONS

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INTRODUCTION

Understanding the complexity of subsurface conditions is paramount in delineating contaminant distribution, developing defensible conceptual site models (CSMs) and implementing sustainable remedies. Despite the decades spent on characterizing DNAPL sites, substantial uncertainty remains in the delineation of DNAPL source zones. Inadequate characterization often results from the use site investigation tools that are not tailored to the scale of subsurface heterogeneity. Historically, DNAPL sites have too often been characterized at a resolution that is insufficient to implement in-situ remedial technologies, however, recent trends propose high resolution site characterization (HRSC) methods with seemingly limitless data densities. Here we introduce the concept of sufficient resolution site characterization (SRSC) that adequately captures the scale of heterogeneity that controls contaminant distribution, fate and transport, and ensures the design and implementation of effective remedies. The SRSC methodology, which is developed in recent best-practice guidance, is illustrated by reference to a detailed case study.

TOOLS AND TECHNIQUES

Recent guidance from the Interstate Technology & Regulatory Council (ITRC, 2015) on DNAPL site characterization provides a systematic approach to site characterization. This best-practice guidance document discusses data adequacy, based on the project objectives and the scale of resolution of data required characterize the site and design and implement a remedy. Central to this guidance is the development of a Tool Selection Worksheet, which assists in the selection of a parameter-driven suite of tools to characterize the subsurface. Over 100 tools are contained in the Tool Selection Worksheet, and selecting various search parameters reduces the list of tools that are applicable to a specific site. The Tool Selection Worksheet is downloadable, and each tool links to additional resources that describe the applicability, advantages, and limitations of each individual tool.

CASE STUDY

Current and emerging site characterization tools were selected for a remedial investigation based with the objective of optimizing the footprint of an in-situ thermal remedy at a coal tar DNAPL site. The specific objectives of the remedial investigation were to i) delineate the spatial distribution of the coal tar DNAPL, ii) quantify uncertainty in DNAPL volume and mass estimates and iii) identify site characterization tools that could be used to design and assess the performance of the thermal remedy. The elements of the remedial investigation program included a novel cost benefit optimization routine to select the sampling density, real-time analysis of site data via a GIS-based data management platform, and data visualization in a 3D modeling environment to quantify contaminant distribution.

SUMMARY AND RECOMMENDATIONS

Sufficient Resolution Site Characterization (SRSC) within an objective-based remedial investigation framework can significantly reduce uncertainty in the delineation of DNAPLs and ensure the successful implementation of in-situ remedies at DNAPL sites. The use of the ITRC Tool Selection Worksheet, the key tools selected for the remedial investigation, the optimization of a real-time site characterization using adaptive sampling methods, and the outcome of the investigation in meeting site specific remedial objectives will be discussed.

REFERENCES

ITRC (Interstate Technology & Regulatory Council). 2015. Integrated DNAPL Site Characterization and Tools Selection (ISC-1). Washington, D.C.: Interstate Technology & Regulatory Council, DNAPL Site Characterization Team. www.itrcweb.org/DNAPL-ISC_tools-selection

HIGH RESOLUTION SITE CHARACTERIZATION: THE PATH TO SUCCESSFUL REMEDIES AND REDUCED COST

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The passage of CERCLA in the United States in 1980 created, nearly instantly, what is today a $9 billion annual industry in that country which is still growing. Knowledge of the fate and transport of industrial chemicals in the subsurface was extremely limited in the 1980s and most of the early practitioners in the new industry came from, or were influenced by, the water supply and wastewater disposal fields. The conceptual models and scales of measurement from these fields were inappropriate for assessment and remediation of chemicals in the subsurface as recognized by a few early pioneers like C.V. Theis and John Cherry. These models and approaches became embedded in the field and are still prevalent today. In the 1980s, pumping and treatment (P&T) of groundwater comprised between 80% and 90% of Superfund groundwater remedies. In large measure these remedies failed to meet the goal of aquifer restoration and as of 2011 P&T comprised only 20% of remedies. Understanding of the nature of contaminant behavior in the subsurface has increased tremendously, largely due to academic research, and new, more effective investigatory and remedial technologies have been developed. The 14th Edition of the Superfund Remedy Report (November 2013) stated that "…the continued increase in the selection of in situ groundwater technologies suggests a role for recently-developed characterization techniques, such as high-resolution site characterization (HRSC)". HRSC has great promise to shorten project life cycles, improve Conceptual Site Models, increase remedy effectiveness and reduce life cycle costs.

Data which are Insufficient in terms of quantity, proper placement and sample scale (usually too large) lead directly to erroneous Conceptual Site Models which in turn lead to bad decisions and remedies that either don't work, underperform or are overdesigned. These situations result in the waste of money and other resources, a lack of protectiveness, as well as failing to alleviate the owner's liability.

HRSC requires making measurements at scales that encompass the spatial structure of the key variables (e.g., hydraulic conductivity, hydraulic head, contaminant concentration, geochemistry etc.), and while direct sensing tools are an important part of HRSC, these tools alone are insufficient. HRSC requires small sampled volumes and close sample spacing of both high and low permeability media, in the source zone and in the dissolved plume. It may be necessary to identify all of the contaminant phases: Non Aqueous Phase Liquid (NAPL), solute, gas and sorbed.

It is critical that data sets provide clear insight into the mechanisms sustaining the plume. For example, is NAPL still present in the source zone? If so, where is it located and how much is present in a relative sense? Is a significant quantity of contaminant mass present in the immobile pore water in low permeability layers within the flow system? If so, is this mass located throughout the footprint of the dissolved plume? What fate mechanisms are significant: biodegradation, abiotic degradation, hydrodynamic dispersion, retardation etc.?

HRSC is best applied using transects normal to the direction of transport. Application of Triad Approach principles reduces the time and costs associated with HRSC. This means using real time measurement tools, managing and interpreting data in near real time, using dynamic work strategies and a life cycle CSM. Another important concept borrowed from the Triad Approach is the use of collaborative data platforms. This essentially means using screening level toos such as MIP and LIF to reduce the overall spatial uncertainty associated with the data and then using definitive tools such as the WaterlooAPS, soil coring and onsite laboratory analyses to manage the analytical uncertainty and the relational uncertainty. This approach can both speed up site characterization and lower the cost.

Appropriate use of technologies such as Waterloo^{APS}, Membrane Interface Probe, LASER Induced Fluorescence, on-site laboratories, geophysical techniques, detailed chemical profiling of aquitard materials and others facilitate the collection of the types and density of data which allow for the level of understanding of site conditions which is required for successful and cost effective selection, design and implementation of the combinations of remedial technologies required to meet remedial goals. In addition, the ability to adequately determine the flux of contaminant mass across key planes is taking on greater importance in terms of assessing the effectiveness of remedies as well as assessing the level of risk posed to potential receptors. Research has shown that the vast majority (e.g., 75%) of contaminant mass flux occurs through a very small portion (e.g., 5 to 10%) of the plume cross sectional area. Identifying these zones allows for targeted remedial efforts to control mass transport, both reducing cost and increasing protectiveness.

HRSC results allow for more “surgical” application of remedial technologies thereby making remedies more cost effective. However, application of a single “high resolution” technology does not result in a high resolution investigation. Multiple tools and techniques are required to address the various questions posed by a given site.

LNAPL TRANSMISSIVITY – WHEN TO USE IT AND A NOVEL WAY TO REFINE VOLUME ESTIMATES

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INTRODUCTION

In the presence of Light Non-Aqueous Phase Liquids (LNAPL) within the subsurface at contaminated land sites, two typical questions are raised:

1. Is the LNAPL migrating? and
2. How much LNAPL is there in the subsurface?

LNAPL transmissivity (Tn) is a measure of the ability of the formation to transmit LNAPL and is dependent on formation properties, LNAPL physical properties, saturation and LNAPL thickness and therefore considered a reasonable measure of the potential for plume migration in many instances. Although Tn can be readily estimated based on measurements of LNAPL drawdown and recharge to the well as a function of time following LNAPL extraction (LNAPL Baildown Tests), its use as a remediation metric is not always applicable.

Estimation of the volume of LNAPL within the subsurface requires knowledge of the formation properties (porosity, van Genuchten parameters, etc.) and LNAPL saturation. The formation properties can either be gathered from literature sources, which may not be as accurate, or through the expensive use of coring and fluorescence techniques.

This presentation aims to discuss the applicability of using Tn and to present a novel method of utilising Tn data to refine LNAPL volume estimates in the absence of expensive investigative techniques.

METHODS

Calculating LNAPL Transmissivity

To determine the Tn, LNAPL baildown tests were completed and based on measurements collected during the baildown tests, Tn was estimated utilising the American Petroleum Institute (API 2012) LNAPL transmissivity spreadsheet.

Modelling LNAPL Volume

The volume of LNAPL was modelled using the LNAPL Distribution and Recovery Model (LDRM) published by the API (API Publication 4760, January 2007).

Based on the input values, the LDRM computes and provides outputs for the following key parameters:

- Total specific LNAPL volume (m^3/m^2) (Dn);
- Recoverable specific LNAPL volume (m^3/m^2) (Rn); and
- LNAPL Transmissivity (m^2/day) (Tn).

The initial modelling utilised literature values for the formation parameters to provide a first pass estimate prior to refinement based on the field measured Tn.

Once the total specific and recoverable specific volumes are modelled, the data can be used to interpolate the volumes present within the subsurface using a spatial program (ArcGIS).

RESULTS AND DISCUSSION

LNAPL baildown tests were conducted on four (4) wells across the site. The results of the Tn analysis is summarised in Table 1 below.

Table 1. Summary of Tn Analysis

Well #	Initial LNAPL Thickness (m)	Initial In-Bore LNAPL Volume (L)	LNAPL Volume Removed (L)	Tn (m^2/day)
1	0.32	0.94	1.8	1.10×10^{-2}
2	0.44	1.31	2.6	2.17×10^{-2}
3	0.27	0.82	1.0	8.97×10^{-2}
4	0.48	1.45	2.5	4.61×10^{-2}

Literature values were initially used in the volume estimate modelling prior to refinement using the Tn data. The different modelling outputs are presented in Table 2 below.

Table 2. Comparison of Modelled Total Volumes

Well #	LNAPL thickness (m)	Bore Log Soil Type Description	Tn – Field (m^2/day)	Tn – Calculated Using Literature Values (m^2/day)	Dn – Calculated Using Literature Values (m)	Dn – Refined Values (m)
1	0.32	Sandy Clay	1.10×10^{-2}	1.5×10^{-2}	0.007	0.007
2	0.44	Silty Clay	2.17×10^{-2}	2.0×10^{-5}	0.000	0.010
3	0.27	Sandy Silty Clay	8.97×10^{-2}	4.6×10^{-3}	0.006	0.015
4	0.48	Sandy Clay	4.61×10^{-2}	4.9×10^{-2}	0.019	0.022

As can be seen in Table 1 above, the LNAPL transmissivities indicate the LNAPL at this site has the potential for further lateral migration (Tn values above our adopted potential mobility guideline of 9.29×10^{-3} m^2/day – ITRC 2009).

Although Tn is now commonly used as a remediation metric whereby an argument can be made to cease active remediation, it is not always suitable depending on the geology. For example, in a fractured rock environment, LNAPL occurrence is governed by the presence of the larger fracture zones. Once these larger fracture zones are depleted of LNAPL via pumping, the rate of LNAPL recovery is governed by the rate of LNAPL recharge by the less continuous and smaller fracture network. If baildown tests are conducted once the larger fracture zone is allowed to be replenished of LNAPL, the Tn measurement will likely be unchanged regardless of the degree of LNAPL previously removed given the generally high connectivity of the larger fractures. At this study site, the geology is considered vertically uniform at each individual bore, thus the above storativity issues are not encountered and Tn is considered a useful remediation metric.

As can be seen in Table 2, the refinement of the modelling of LNAPL volumes (total and recoverable) can be readily conducted. Previously, the refinement of the volume estimate would require freezing cored soil samples for overseas laboratory analysis via fluorescence which is typically cost prohibitive.

CONCLUSIONS

LNAPL transmissivities calculated from field measurements can be readily utilised to refine LNAPL volume estimate modelling exercises.

REFERENCES

Charbeneau, R.J. et. al. (2012) *A User Guide for API LNAPL Transmissivity Spread sheet: A Tool for Baildown Test Analysis. (Draft)*

Charbeneau, R.J. (2007) *API Publication 4760: LNAPL Distribution and Recoverability Model (LDRM) Volume 1: Distribution and Recovery of Petroleum Hydrocarbon Liquids in Porous Media.*

Interstate Technology and Regulatory Council (ITRC) (2009) *LNAPLs Team Evaluating LNAPL Remedial Technologies for Achieving Project Goals.*

REVIEW OF CHARACTERIZATION METHODS FOR NAPL SOURCE ZONE DELINEATION AND MASS ESTIMATION

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INTRODUCTION

Delineation of the horizontal and vertical extent of NAPL source zones is required when in-situ source treatment is to be implemented at a site. Estimation of NAPL mass may be helpful at some sites for evaluating remediation timeframe and tracking remedial progress. These two characterization goals are both challenging to implement at typical NAPL sites, particularly when NAPL is sparsely present or is not readily observed in soil cores. This review presents various methods available for NAPL source zone delineation and mass estimation, including several case studies to demonstrate the efficacy of these methods.

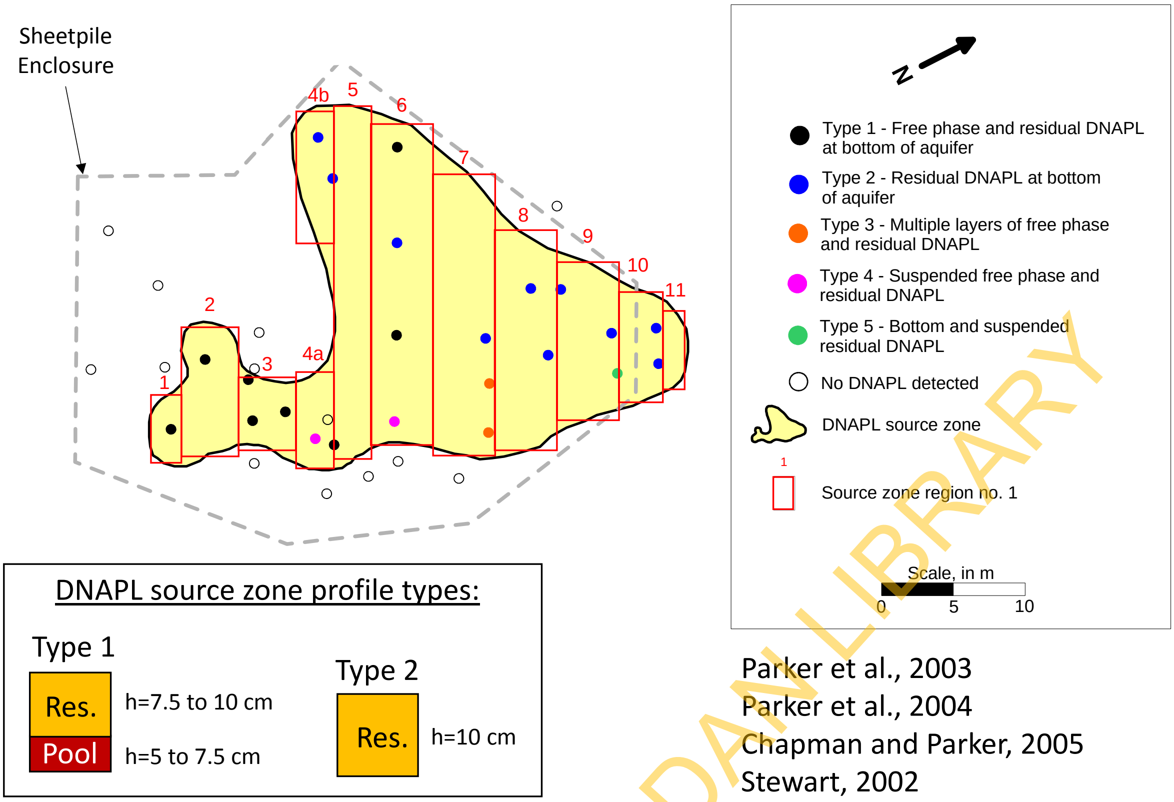
NAPL Source Zone Delineation

ITRC (2015) provides valuable guidance for the selection of data collection tools which may be useful for field investigations at DNAPL sites. Kueper and Davies (2009) present a lines-of-evidence approach to delineate the overall extent of potential and/or confirmed NAPL source zones, based on NAPL indicators determined from field and other site data. The strengths and limitations of various NAPL indicators are discussed for single and multicomponent NAPL, including observed (or the lack of visible) NAPL, soil concentrations that exceed either the saturation or partitioning thresholds, groundwater concentrations exceeding 10% or 1% of solubility, dye tests, stains or sheens with supporting evidence, and other potential indicators. Lines of evidence which may be used to indicate the presence of pooled (i.e. free phase) NAPL are presented. A case study of NAPL delineation based on data presented in Parker et al. (2003, 2004), Chapman and Parker (2005), and Stewart (2002) is discussed (Figure 1). The benefits of high resolution characterization of spatially varying NAPL architecture are demonstrated based on this case study. The benefits and limitations of a more simple delineation of the overall horizontal and vertical extent of a NAPL source zone are reviewed.

Estimation of Readily Accessible NAPL Mass

Estimating NAPL mass in the subsurface will implicitly have high uncertainty. Regardless, this metric may still prove useful for some sites as discussed above. Benefits and limitations of various methods for estimating NAPL mass are reviewed, including partitioning interwell tracer tests (PITT), bulk retention capacity, and high resolution characterization of NAPL architecture variations in a source zone. A review of field-scale case studies where NAPL mass was estimated based on these three approaches is presented.

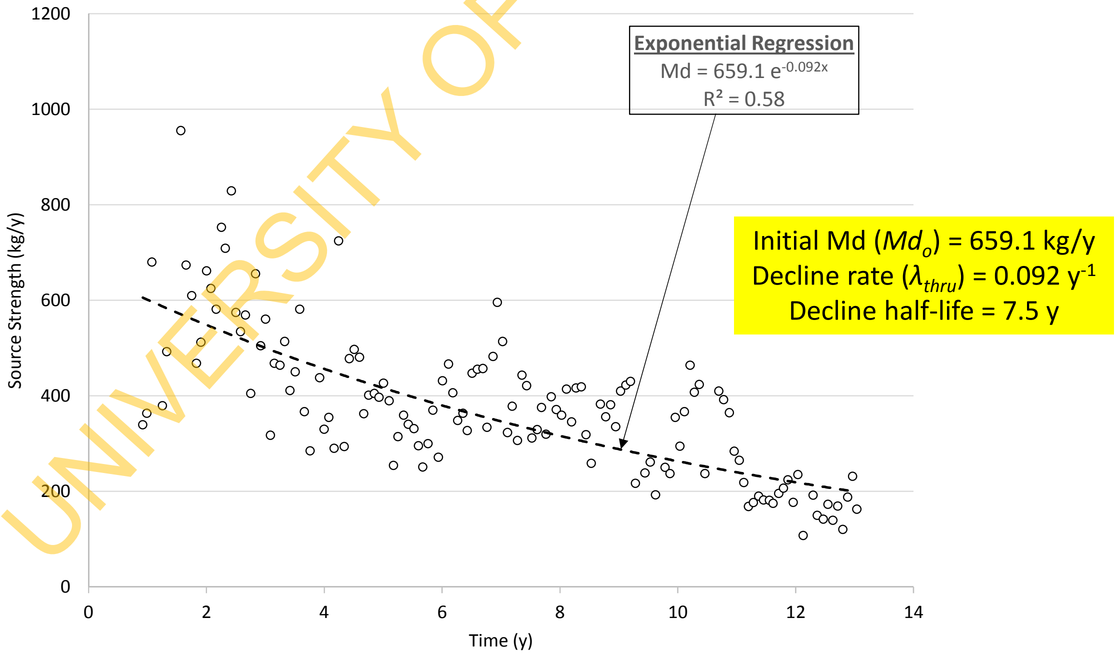
A relatively simple method for estimating readily accessible NAPL mass is also discussed, based on the ratio of initial source strength (i.e. mass discharge) and the exponential rate of decline of source strength over time. These data are typically available at sites with existing pump-and-treat systems in place for source containment. An example case study is presented based on data in Brusseau et al. (2011) for an Arizona site (Figure 2). Based on the estimated initial source strength (659 kg/y) and the rate of source strength decline (0.092 per year, or a half-life of 7.5 y), the initial readily accessible NAPL mass in the subsurface is estimated to be 7,200 kg. Limitations associated with this simple method are discussed.



Parker et al., 2003
Parker et al., 2004
Chapman and Parker, 2005
Stewart, 2002

Fig. 1. Delineation of DNAPL source zone and sub-zones at Connecticut Site.

Note: Source strength = mass discharge (Md) at downgradient source zone boundary.



Initial Md (Md_o) = 659.1 kg/y
Decline rate (λ_{thru}) = 0.092 y^{-1}
Decline half-life = 7.5 y

Fig. 2. Approximation of readily accessible DNAPL mass at Arizona Site. Data modified from Brusseau et al. (2011).

INTEGRATED DNAPL SITE CHARACTERIZATION AND TOOLS SELECTION

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INTRODUCTION

Sites contaminated with dense nonaqueous phase liquids (DNAPLs) and DNAPL mixtures present significant environmental challenges. Despite the decades spent on characterizing and attempting to remediate DNAPL sites, substantial risk remains. Inadequate characterization of site geology as well as the distribution, characteristics, and behavior of contaminants -- by relying on traditional monitoring well methods rather than more innovative and integrated approaches -- has limited the success of many remediation efforts.

METHODS

The Integrated DNAPL Site Characterization Team has synthesized the knowledge about DNAPL site characterization and remediation acquired over the past several decades, and has integrated that information into a new document, Integrated DNAPL Site Characterization and Tools Selection (ISC-1, 2015). This guidance is a resource to inform regulators, responsible parties, other problem holders, consultants, community stakeholders, and other interested parties of the critical concepts related to characterization approaches and tools for collecting subsurface data at DNAPL sites.

RESULTS AND DISCUSSION

After this associated training, participants will be able to use the ITRC Integrated DNAPL Site Characterization and Tools Selection (ISC-1, 2015) guidance to develop and support an integrated approach to DNAPL site characterization, including:

- Identify what site conditions must be considered when developing an informative DNAPL conceptual site model (CSM)
- Define an objectives-based DNAPL characterization strategy
- Understand what tools and resources are available to improve the identification, collection, and evaluation of appropriate site characterization data
- Navigate the DNAPL characterization tools table and select appropriate technologies to fill site-specific data gaps

CONCLUSIONS

This talk will present a condensed version of the free 2.5 hour internet seminar that is currently being offered by the DNAPL Site Characterization team.

STATE OF THE ART IN DEVELOPING CONCEPTUAL SITE MODELS FOR DNAPL GROUNDWATER PLUMES

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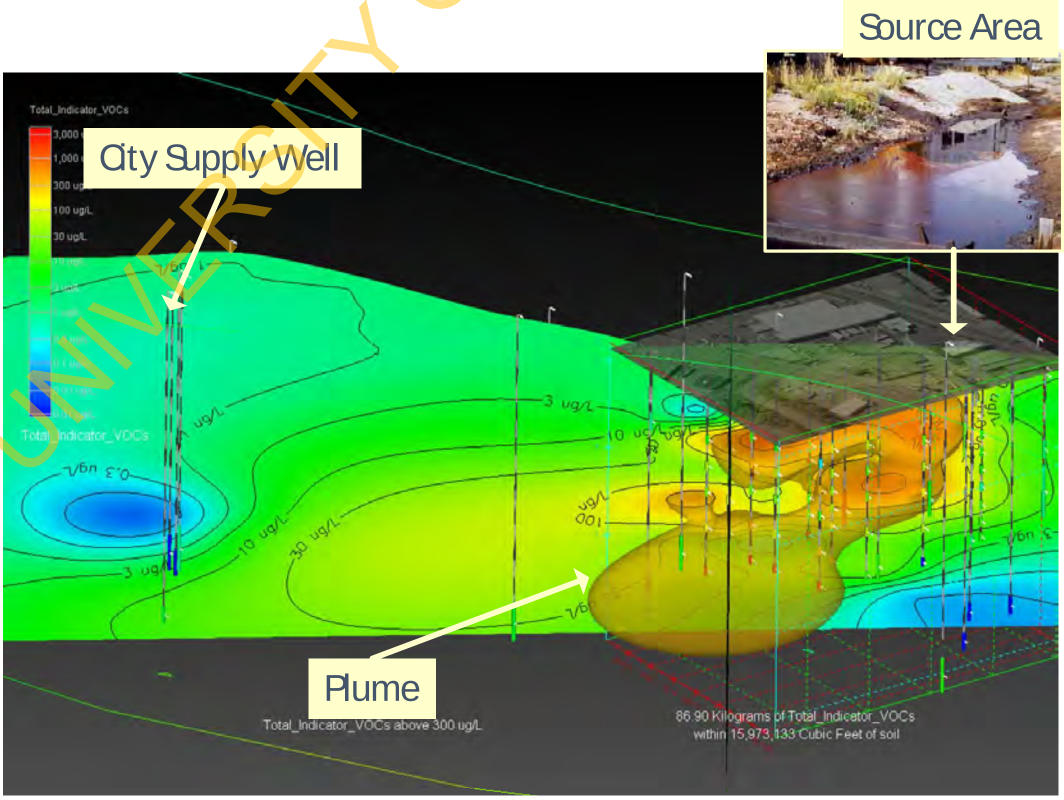
INTRODUCTION

Over the last decade, improved characterization and modelling tools have facilitated development of more robust conceptual site models (CSMs) for dense non-aqueous phase liquid (DNAPL)-contaminated groundwater aquifers which describe complex phenomena, such as heterogeneous distribution and transport, back diffusion, and multi-phase contaminant flux and attenuation. In addition, innovations in the state of the practice and lessons learned from sites which have been undergoing remediation for decades has significantly improved technical and logistical knowledge which can be leveraged to develop more cost-effective, and realistic, management plans acceptable to stakeholders and decision-makers. First, a more holistic conceptualization of DNAPL sources and plumes as dynamic systems can be achieved with new, innovative tools and technologies that more accurately measure phenomena such as groundwater hydraulics, chemical diffusion and aquifer biogeochemical conditions which often vary over space and time and dictate which attenuation mechanisms are prevalent throughout the plume. New characterization technologies also allow for elucidation and modeling of biotic and abiotic contaminant degradation mechanisms including more obscure reactions relevant over the timescales that the plume is undergoing restoration. Finally, advances in contaminant fate and transport modeling allow for integration of contaminant degradation reactions, geochemical conditions and hydraulic field measurements for quantitative assessment of contaminant fate resulting in more accurate predictions of contaminant mass flux and discharge and concentrations over relatively long restoration timescales.



INNOVATIONS IN TOOLS AND TECHNOLOGIES

An overview of the state of the art in characterizing DNAPL sites and developing robust conceptual site models will be described that includes the latest developments in technologies and tools available to practitioners, stakeholders and responsible parties. First, state of the art diagnostic and prognostic tools have been developed to assess *in situ* contaminant degradation within the aquifer. Innovative tools discussed will include the use of molecular biological tools to characterize contaminant degradation mechanisms and rates including compound specific isotope analysis (CSIA) and DNA- and RNA-based assays to characterize and quantify microbial communities capable of biodegrading chemicals in aquifer systems. In addition, advances in the understanding of abiotic degradation mechanisms will be provided which have proved especially important in attenuating diffused contaminants in sedimentary bedrock. Integrating knowledge of degradation with prevalent geochemical conditions allows for "mapping" degradation across the extent of contaminant plume and accounts for changing conditions over time and space. This provides a framework to understand the environmental response to the presence of contaminants and the need to provide intervention to address risk to human health and the environment.

Second, significant advances have been made in tools available to characterize the DNAPL plume distribution and architecture in the subsurface, including the impact of system heterogeneity on DNAPL plume persistence. DNAPL residual may persist at the interface between sediment types with contrasting permeability. Diffusive interchange between higher and lower permeability zones slows the propagation of dissolved phase contaminants during early stages of plume development; then sustains the dissolved phase concentrations over extended periods due to chemical diffusion. High resolution profiling tools are now available that allow for quantification of contaminant mass and extent on a relevant geologic scale to quantify significant characteristics, such as presence and saturation of DNAPL, and significance of matrix diffusion.

Lastly, new modelling tools are available that allow for visualization, and quantification of complex subsurface DNAPL plumes. Visualization models allow for integration of complex data sets including geologic sediment and/or rock zones and interfaces, groundwater characteristics, contaminant distribution in soils, groundwater and soil gas, and spatial relationships to receptors. These can be used to quantify contaminant mass, define remediation treatment zones, and convey the conceptual site model to stakeholders. Numerical contaminant fate and transport models have also developed capable of integrating geochemical, biotic and abiotic contaminant degradation and to account for matrix diffusion to understand current conditions and predict future evolution and persistence of the DNAPL plume. They can also be used to predict the impact of potential cleanup strategies.

A discussion of the state of the art will include examples of how these new tools are being used for cleanup of contaminated sites in the United States and provide an overview of new regulatory guidance documents, webtools and training available to educate regulatory agencies on these new innovations through the Intrastate Technology Regulatory Council (http://www.itrcweb.org/). Successes and lessons learned will also be provided.

AQUIFER TESTING TO DETERMINE BEDROCK ANISOTROPY AND LNAPL FLOW PATHWAYS

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INTRODUCTION

Fluorescein tracer injection and monitoring and a sustained drawdown pumping test were undertaken in a fractured bedrock aquifer. The objective was to determine whether the heterogeneity of the bedrock aquifer, comprising alternating north-south trending quartzite and siltstone bands, created an anisotropic groundwater flow regime.

Background

Past investigation showed that LNAPL and dissolved-phase hydrocarbons were present in a shallow fractured bedrock aquifer at a site located adjacent to the ocean. The bedrock comprised alternating north-south trending bands of fractured siltstone and quartzite, with the LNAPL contained within one quartzite band. LNAPL thicknesses had decreased and routine monitoring did not indicate migration towards the ocean. It was hypothesised that the heterogeneity and anisotropy of bedrock was the primary influence on LNAPL migration, with the quartzite creating a preferential flow pathway inducing migration parallel to the shoreline.

METHODS

Fluorescein Tracer Injection and Monitoring

Fluorescein dye was injected into a purpose-designed pumping/injection well (PW001) located along the quartzite band where LNAPL was present. The tracer was injected as a slug followed by flushing of the well using 600L (5 well volumes) of tap water.
Groundwater quality monitoring was undertaken at a selected monitoring well network prior to and after the tracer injection to determine background and post-injection fluorescein concentrations. Monitoring ceased after 14 weeks post-injection. Carbon samplers were deployed for either one or two week intervals, with a grab sample collected at the end of each carbon sampler interval. Field staff undertook visual sample inspection for evidence of fluorescein (using a torch in a dark room). Grab and carbon samples were shipped to Ozark Laboratories in the US for Fluorescein analysis.

Sustained Drawdown Pumping Test

At the conclusion of fluorescein monitoring a sustained drawdown pumping test was conducted on PW001. A pneumatic, submersible pump sustained approximately 3.5m of drawdown within PW001 for a 48 hour period. Barometric pressure and water level were measured in PW001 and the selected monitoring well network including at one background well monitoring for tidal influence. Transducers were deployed two days prior to the test and removed after 90% recovery was noted in all wells. Throughout the test, flow rate was monitored using an in-line cycle counter with the volume per discharge cycle measured using a volumetric container.
Data were filtered for tidal influence using a moving average method (Serfes, 1991) and analysed using a distance-drawdown plot (Powers, 1997) and the Cooper-Jacob (1946) solution.

RESULTS AND DISCUSSION

Fluorescein Tracer Injection and Monitoring

Field staff visually identified fluorescein tracer after two days in grab samples collected from GW004, located approximately 7m to the north along strike within the fractured quartzite bed. No other visual detections were noted along or across the strike of the quartzite band. The early fluorescein detection in GW004 was potentially due to artificial mounding created from the injection event at PW001.

Overall, fluorescein concentrations were detected in four wells (Table 1).

Table 1. Maximum detected fluorescein concentrations

Well ID	Distance from PW001 (metres)	Direction from PW001	Elapsed Time (days)	Max. Fluorescein Concentration (ppb)	Screen Lithology (saturated section)	Apparent Velocity (m/day)
GW004	5.35	North	2	20,800	Quartzite	2.7
GW012	14.37	South	94	0.15	Quartz Gravel	0.15
MW335	3.43	West	94	61.9	Quartzite	0.03
MW336	3.39	West	94	17.5	Siltstone	0.03

Results indicated a preferential pathway along the strike of the quartzite band with the apparent velocity at GW012 (along strike) one order of magnitude higher than that at MW335 (quartzite) and MW336 (siltstone), both across strike.

Sustained Drawdown Pumping Test

Data indicated that apparent drawdown occurred in five wells within the quartzite unit (MW335, GW004, MW321, GW007, and GW012) with drawdown ranging from a maximum of 0.59m (GW004) to a minimum of 0.11m (GW012) along strike, with estimated maximum drawdown decreasing with distance away from PW001. MW335, located across strike in the quartzite unit experienced 0.10m. Wells present across strike in the adjacent siltstone unit did not experience drawdown.

CONCLUSIONS

The findings of the tracer and pumping tests were found to be complementary and indicative of the alternative bedrock bands creating anisotropic groundwater flow with groundwater movement impeded by the westerly siltstone unit and moving preferentially north-south along the strike of the quartzite band. Based on these results, LNAPL discharge to the marine environment was not considered to be a potential occurrence.

REFERENCES

Powers, P. J., Corwin, A. B., Schmall, P.C., Kaeck, W. E., (2007) *Construction Dewatering and Groundwater Control, New Methods and Applications*, 3rd Ed., John Wiley and Sons, NJ.

Serfes, M. (1991) Determining the Mean Hydraulic Gradient of Groundwater Affected by Tidal Fluctuations, *Groundwater* Vol. 29, No. 4, July-August 1991.

Cooper, H.H. and C.E. Jacob, (1946) A generalized graphical method for evaluating formation constants and summarizing well field history, *Am. Geophys*. Union Trans., vol. 27, pp. 526-534.

CROSSING THE GAP:
STAR TREATMENT OF HETEROGENOUS NAPL DISTRIBUTION

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INTRODUCTION

STAR is an innovative, patented and patent pending thermal technology based on the principles of smouldering combustion, where the contaminants are the source of fuel. The process is self-sustaining following a short duration, low energy ignition event, such that the energy of the reacting contaminants is used to pre-heat and initiate combustion of contaminants in the adjacent area, propagating a combustion front through the contaminated zone, provided a sufficient flux of air is supplied. The porous media is key to maintaining the STAR reaction as it helps hold and recycle the released energy. However, heterogeneous and discontinuous distributions of the fuel, with relatively clean gaps of various lengths between zones of higher concentrations, can form in the subsurface after the contaminant is released and may act as a barrier to continued combustion propagation without re-ignition at a subsequent location.

The purpose of this study was to evaluate the: (1) maximum clean gap thickness through which a smouldering propagation front could continue; (2) the influence of multiple gaps on propagation; (3) gap thickness as a function of key parameters (i.e., permeability, water content, Non-Aqueous Phase Liquid (NAPL) saturation and mobility, and air flow rate; and (4) the minimum NAPL “finger” thickness need to support propagation.

METHODS

One dimensional upwards combustion tests were conducted in 15 centimeter (cm) diameter by 15 or 90 cm long columns which contained a heating coil and air diffuser at their base. Coal tar was used as the fuel and was mixed with sand, which was then placed in layers with single to multiple clean sand gaps. Depending on the test conditions, a coarse (16 mesh, 1.2 mm sieve size), medium (20/30 mesh, 0.85 – 0.6 mm sieve size), and fine (100 mesh, 0.152 sieve size) sand was mixed with coal tar to achieve various NAPL saturations (15% to 40%) and water content (0% to 70%). The air flows used ranged between 50 to 150 liters per minute (LPM). To investigate the affect of finger thickness, contaminated, dry, coarse sand (25 % NAPL saturation) was packed in the center of the column as a vertical finger (cylinder) of defined diameter surrounded by clean sand. The diameter of the finger was reduced from the width of the entire column (15 cm) to 7 cm, 5 cm, and 2 cm. Sensitivity to sand type (i.e., the permeability of the sand around the finger) for the 2 cm finger was investigated. For each test, collected data included thermocouple (TC) data (i.e., temperature profiles), combustion gas (carbon monoxide [CO] and carbon dioxide [CO_2]) concentrations in vapor emissions, and photographs of soils before and after STAR treatment. A total of: 12 column tests (including the base case) where used to assess the maximum gap thickness; three (3) tests were used to asses multiple gap tests; nine (9) column tests plus the base case where used to asses the impact of varying parameters of NAPL and water content, sand size and flow rate had on gap thickness propagation; 26 test were used to assess NAPL mobility; and five (5) test were used to asses finger thickness.

RESULTS AND DISCUSSION

The experiments showed that the combustion front can successfully cross clean single gaps up to 40 cm, as well as multiple 12 cm clean gaps, over a variety of NAPL and water saturations, soil permeabilities, and air flows provided that the fuel beyond the gap achieves its ignition temperature (i.e., at least 350 degrees Celsius (°C) for the coal tar used in this evaluation). Meeting the ignition temperature is a function of the amount of energy transmitted into the gap, which is related to the thickness/mass of the preceding smouldering fuel layer. The clean sand stores and transmits by convection and conduction the energy released by the previous layer of smouldering fuel, acting as a thermal battery. Therefore, larger fuel layers (or higher percentage of NAPL) will release more energy, resulting in the propagation of high temperatures longer distances into clean gaps and the subsequent crossing of larger clean gaps.

Air flow played two important functions in the experiments: (1) delivering oxidant required for the combustion reaction; and, (2) controlling the relative rates of heat transfer/losses. Air flow rates that were too high lead to too much cooling of the convected air due to the thermal non-equilibrium between the fuel and the air and the peak temperature decreased rapidly across the gap. As a result, the ignition temperature for the fuel across the gap was not achieved. If the permeability of the materials is too low, then there is insufficient flux of oxygen to support combustion.

NAPL mobilization occurred under various conditions within the column due to the heating and subsequent reduction in viscosity of the NAPL being combusted. The degree of NAPL mobilization is a function of NAPL saturation, permeability, and air flow rate. However, the combined effects of higher air flow rates along with the shorter time to transmit the heat energy limits the time for migration to occur. With all other factors being equal, higher NAPL saturations contribute to higher NAPL mobility. Although NAPL mobility can redistribute the available energy within the gap and enhanced the ability of smouldering to cross clean gaps, numerous experiments showed that substantial gaps can be crossed where there was no significant NAPL migration.

The volume versus surface area of the smouldering region will govern the heat generation and heat losses and, therefore, the minimum finger thickness that will support the self-sustaining nature of the smouldering reaction. Our experiments showed that finger thicknesses of 5 cm (diameter) or greater were successfully smouldered, but 2 cm diameter fingers were not, likely due to an insufficient volume of coal tar at which energy losses to the surrounding clean sand can be overcome to achieve ignition.

CONCLUSIONS

The results show that STAR can be used to treat heterogeneous distribution of NAPLs in the soils over the conditions tested in the column studies. Heat loss across the gap governs if ignition of fuels across the gap will occur. This heat loss will be much greater at the scale of the experiments used for this study, and therefore, the gaps and finger thickness that can sustain STAR *in situ* would likely be much larger with all other conditions being the same.

MODELING LNAPL DEPLETION AT A FORMER XYLENE PROCESSING FACILITY (GERMANY)

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INTRODUCTION

Non-aqueous phase liquids (NAPL) present below the water table will undergo natural depletion because of ongoing dissolution into groundwater. The NAPL Depletion Model (NDM) is a screening-level model that was developed to simulate declining source strength trends for NAPL source zones based on naturally-occurring or enhanced dissolution (Carey et al., 2014a). NDM is a public domain model and is available for download at www.porewater.com. NDM was used to simulate LNAPL depletion at a former xylene processing plant in the lower Rhine area in Germany, over a period of 4.5 years during operation of a groundwater extraction system. Schafer and Therrien (1995) previously used a sophisticated three-dimensional reactive transport model to simulate the xylene plume derived from a residual LNAPL source zone that is approximately 120 m long and 70 m wide. Based on their modeling work, Schafer and Therrien (1995) determined that vertical transverse dispersivity and the LNAPL penetration depth into the aquifer were critical parameters which influenced the simulated source strength (and thus the rate of LNAPL dissolution). This is consistent with the occurrence of both surface discharge (Md_{surf}) due to dissolution at the lower LNAPL surface, and through-discharge (Md_{thru}) as groundwater flows through the LNAPL zone (Figure 1). Schafer and Therrien used their model to calibrate a transverse dispersivity of 10 mm, which is 20 to 50 times larger than anticipated based on measured values at other sites. There were not sufficient field data available for the characterization of LNAPL architecture and smear zone thickness.

MODELING APPROACH

NDM was used to compare the relative magnitudes of surface and through-discharge for the xylene LNAPL source zone based on an alternative conceptualization, using a much smaller transverse dispersivity value (0.22 mm) based on the regression equation derived in Carey et al. (2015), and a larger effective thickness for the LNAPL smear zone (1.7 m, versus 0.17 m that was used in the original study). The thicker smear zone is consistent with the large drop which occurred in the water table elevation over the remediation period, during which significant xylene dissolution was still occurring.

The simple 1-D screening level model (NDM) incorporated 20 grid cells, to allow for simulation of the influence of depleting source zone length on the dissolution rate. The observed mass discharge was estimated based on data presented in Schafer and Therrien (1995). An exponential decline term was derived to represent the declining through-discharge rate based on the observed decline in water table elevation (Figure 2). Calibration was not required for the NDM simulation because input parameters were site-specific, or estimated with regression equations based on hydraulic conductivity (e.g. Carey et al., 2015).

CONCLUSIONS

NDM was demonstrated to be a valuable tool for improving our understanding of site factors which influence NAPL depletion, refining the NAPL architecture characterization, and for comparing the relative benefit of enhanced versus naturally-occurring NAPL dissolution. Through-discharge was shown to be initially the dominant dissolution process, with declining influence as the water table declined. Figure 3 illustrates that there is a relatively good match between the observed and modelled mass discharge (i.e. dissolution rate), which validates this alternative architecture conceptualization (i.e. low transverse dispersivity and initially thick smear zone). Also, the use of pump-and-treat is shown to increase the xylene

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LNAPL dissolution rate by 100% (Figure 3). This supports the use of strategic pump-and-treat (SP&T) as a treatment technology for LNAPL, as discussed in Carey et al. (2014b).

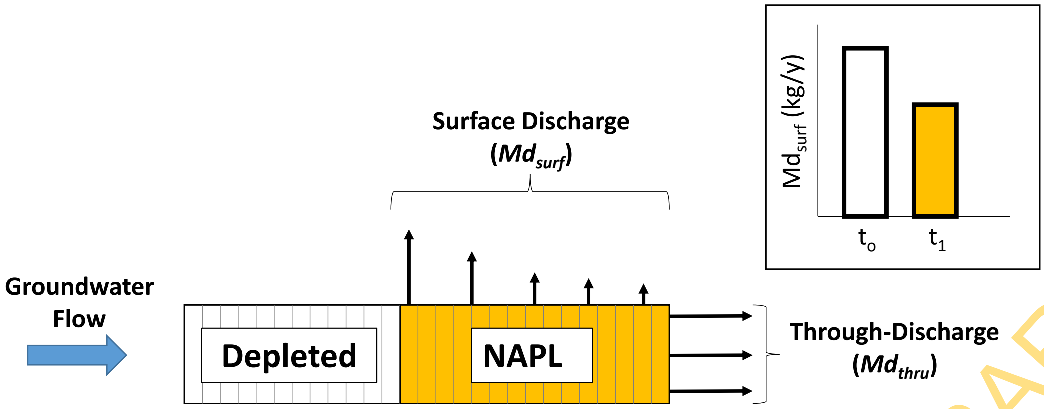

Fig. 1. NDM conceptualization of mass discharge components for LNAPL dissolution.

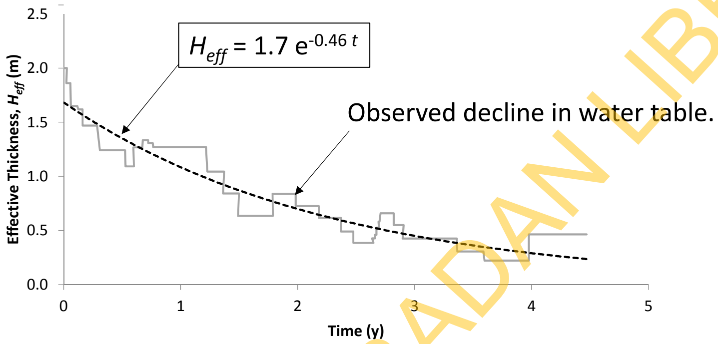

Fig. 2. Fitting of an exponential decline model for effective NAPL source zone thickness, based on the declining water table elevation.

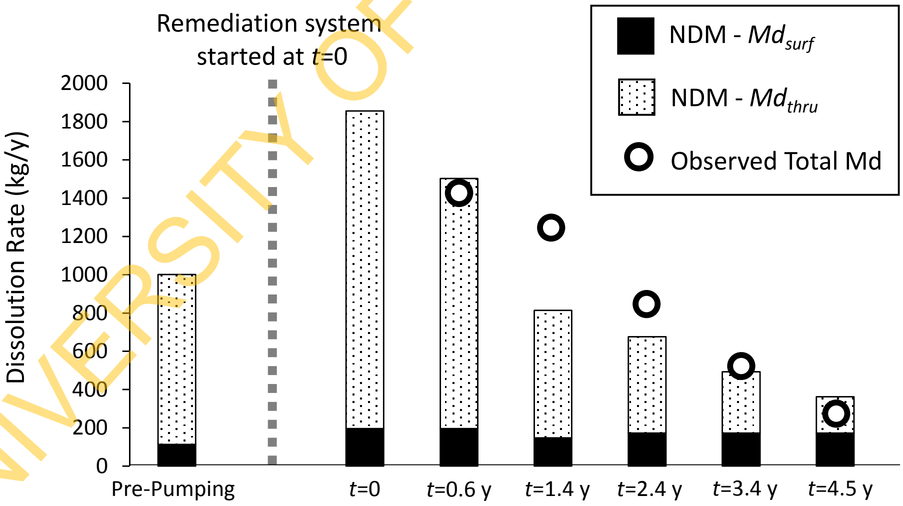

Fig. 3. Observed and modelled mass discharge trends.

REFERENCES

Carey, G.R., McBean, E.A., Feenstra, S. (2014a) DNAPL source depletion: Predicting rates and timeframes. Remediation J., Summer 2014.

Carey, G.R., McBean, E.A., Feenstra, S. (2014b) DNAPL source depletion: Attainable goals and cost-benefit analyses. Remediation J., Fall 2014.

Carey, G.R., McBean, E.A., Feenstra, S. (2015) Estimating Vertical Transverse Dispersivity Based on Hydraulic Conductivity and Groundwater Velocity. In preparation.

Schafer, W. and Therrien, R. (1995) Simulating transport and removal of xylene during remediation of a sandy aquifer. J. of Contaminant Hydrology, 19: 205-236.

RECONSTRUCTING THE RELEASE AND LONGEVITY OF LNAPL PETROLEUM FUEL IN THE FACE OF LIMITED DATA USING A MULTI-COMPONENT, MULTI-PHASE MODELLING APPROACH

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INTRODUCTION

We aimed to quantify the possible scales of previous LNAPL petroleum fuel releases (mainly gasoline) into the subsurface at a site with a paucity of information on the possible sources and timing of releases. These incidents occurred prior to or around the late 1990s. Previous studies during the period from 1998 to 2007 and the more recent site investigation in 2014 were considered in framing the simulations used to elucidate the location and scale of the releases along with the fate of the source and dissolved petroleum hydrocarbons in the groundwater at the site.

METHODS

None of the previous investigations attempted to reconstruct the sources of the fuel releases at the site. This limits the validity of attempts made to predict the fate of the contaminants and the longevity of the effects of the contamination on local groundwater on simplistic boundary conditions and simple solute transport models. Here we used a multi-component multi-phase, modelling approach to capture the essential physics of the contaminant behaviour in an attempt to identify the location and size of the fuel releases. A multi-component multi-phase, study was pursued using the TMVOC simulator. We considered the 16 most critical constituents of gasoline (as the most probable released LNAPL) in simulating the dynamics of the LNAPL source as well as the partitioning of LNAPL components into different phases. The lack of some critical information plus the highly non-linear nature of the problem caused ambiguities in the modelling process. However, we could reconstruct three feasible release scenarios (with respect to water table fluctuations and the released mass) based on the history of dissolved contaminants in groundwater (Figure 1). We also considered the expected composition of these contaminants in the late 1990s.

RESULTS AND DISCUSSION

A lack of information on the representativeness of the historical contaminant groundwater concentrations created ambiguities in reconstructing the history of LNAPL releases. Despite this we showed that various release scenarios could mimic the observed dissolved concentrations in groundwater. For instance, Figure 2 provides a comparison of the modelled and observed BTEX concentrations in the aqueous phase in one of the observation wells for the three scenarios. The results also revealed the remained mass up to the present date would vary significantly with the different scenarios.

CONCLUSIONS

The study indicates that prediction of contaminant longevity is considerably more complicated than the level of the complexity applied in previous modelling studies using solute transport models. Therefore, it is strongly recommended that multi-phase and multi-component modelling approaches such as that used here be used for similar cases. Also it is evident that for this and similar LNAPL release incidents, the lack of specific input data and a well-defined conceptual site model exacerbates the nonlinearity and non-uniqueness of the problem leading to different possible scenarios producing similar observations. Therefore

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results from the modelling need to be used in conjunction with any complementary evidence in order to determine the most likely release and fate scenarios.

REFERENCE

Pruess, K., Battistelli, A., April 2002. TMVOC, A Numerical Simulator for Three-Phase Non-isothermal Flows of Multicomponent Hydrocarbon Mixtures in Saturated-Unsaturated Heterogeneous Media. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.

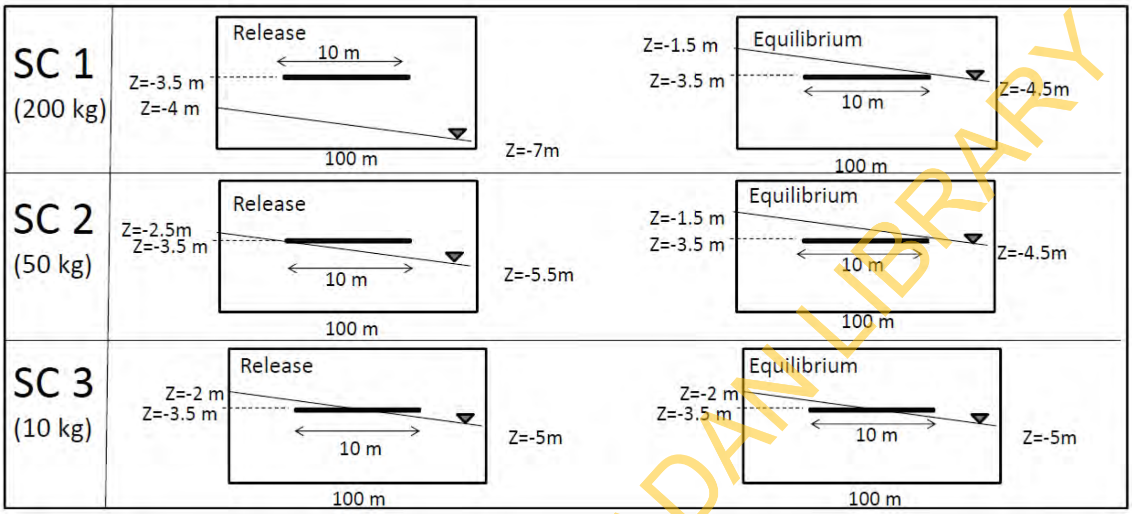

Fig. 1. The three release scenarios showing differing water table elevations and different released masses. Note: SC1 is a 200 kg release, SC2 is a 50 kg release and SC3 is a 10 kg release.

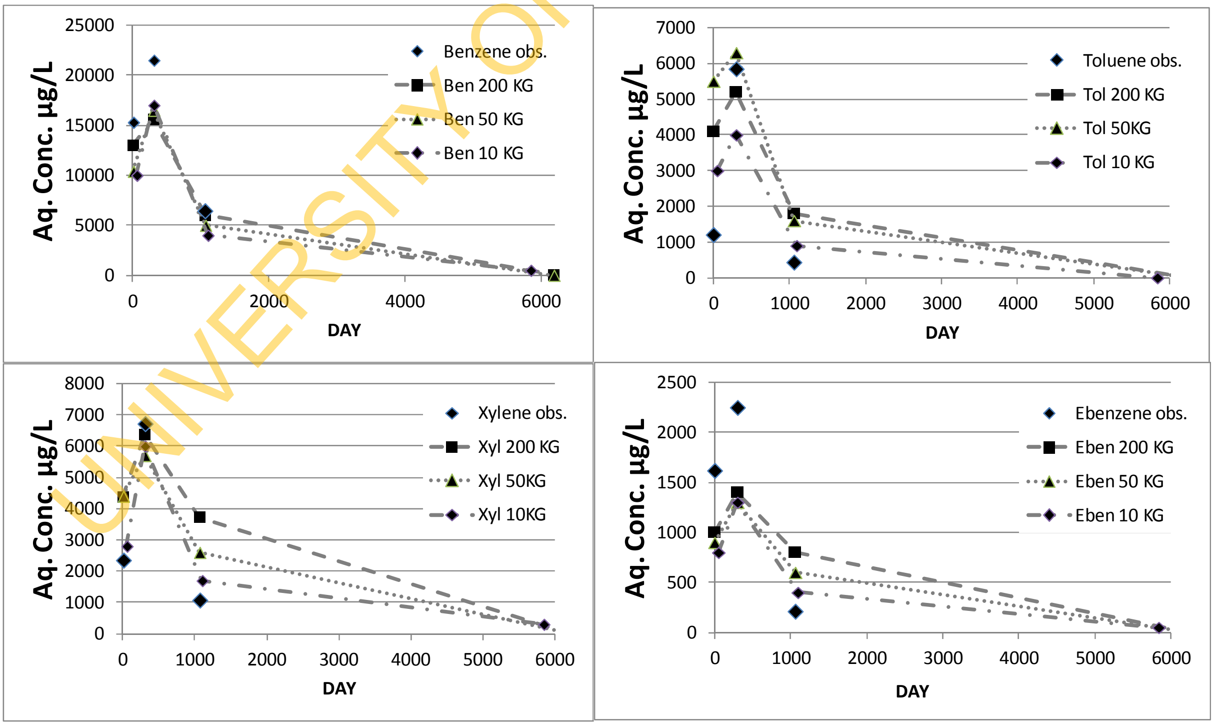

Fig. 2. Comparison of observed BTEX concentrations in the aqueous phase with simulated values from the three scenarios.

USE OF LNAPL TRANSMISSIVITY METRICS FOR LNAPL REMEDIATION IN DUAL POSOSITY AND FRACTURED AQUIFERS — A CASE STUDY

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INTRODUCTION

LNAPL remediation in dual porosity and fractured bedrock aquifers is a challenge in both understanding the extent of LNAPL in the subsurface as well as identifying practical and efficient remediation options to remove LNAPL to the extent practicable.

LNAPL transmissivity (Tn) is a useful metric to assess LNAPL abundance, saturation and recoverability, and hence the relative suitability of remedial techniques, as well as the practicability of ongoing remedial activities in accordance with the regulatory guidelines (i.e. Clean Up to The Extent Practicable (CUTEP)).

The American Petroleum Institute (API) Transmissivity Workbook is a widely used method to undertake Tn calculations. However, these calculations may not be accurate in dual porosity aquifers or highly variable strata, such as infilled ground, siltstone, or fractured bedrock such as Victorian basalt. This is due to the assumptions on aquifer hydraulic characteristics underlying the estimation of Tn and practicalities with obtaining and interpreting quality LNAPL recovery data.

This case study outlines the challenges encountered in the use of LNAPL Tn in the development of LNAPL conceptual site models (CSMs) and remediation options at a number of LNAPL remediation sites with dual porosity and fractured aquifers, including the applicability and use of LNAPL Tn calculations as a remediation metric.

METHODS

The methodology comprised the following:

(a) LNAPL pumpout tests were undertaken using peristaltic pumps, whilst LNAPL recovery was measured using interface probes.
(b) A data validation step was undertaken to appraise LNAPL recovery against expected results, non-equilibrium conditions, filter-pack responses, apparent fracture-flow, confined or perched responses and ultimately critique data selection for input into the Tn calculation.
(c) Tn values were calculated and model values adjusted to optimise the calculated Tn against expected results.
(d) Once validated, results were compared against available data on aquifer permeability and porosity, to evaluate correlations with other lines of evidence of aquifer permeability and LNAPL recoverability.

In summary, Tn values calculated using the API workbook varied widely for these aquifer conditions, and calculated results often varied significantly from anticipated results.

As expected, data validation stages identified limitations in the Tn calculations associated with the LNAPL recovery from aquifers with higher heterogeneity in pore spaces and fractured aquifers with preferential flow pathways. Challenges arose from:

(a) Non-equilibrium conditions, in some cases associated with previous remediation activities.

(b) Variable early-time data, indicative of either filter pack responses, variable flow pathways or variable pore spaces in the aquifer.
(c) Data-normalisation issues and challenges with filtering the dataset to eliminate noise and unrepresentative data.
(d) Patterns of LNAPL recharge suggestive of fracture draining, which appeared broadly comparable to a confined-aquifer scenario.
(e) Significant variability in the LNAPL recharge data, considered indicative of the variable recharge patterns associated with fracture dominated flow systems or aquifers with highly heterogeneous pore spaces.
(f) Impact of tidal influences and groundwater fluctuations.

RESULTS AND DISCUSSION

In generating Tn estimates, a detailed stage of data appraisal on a well-by-well basis proved to be essential to critique the LNAPL recharge patterns and select the data likely to be indicative of LNAPL recharge from the aquifer suitable for the Tn calculation. For these aquifer types, the data analysis stages often revealed further detail regarding the LNAPL recharge behaviour, which has proven essential to refine the CSM and characterise the recoverability of LNAPL.

In general, calculated Tn values were considered broadly representative of LNAPL yield and recovery, when compared to field test findings. However, an intensive data interrogation was necessary to quality check the data for inclusion in the Tn calculation. It was also apparent that some datasets were not suitable for Tn calculations, as the calculated values were in excess of expected values. This was often due to variable recharge patterns and/or late-time recharge data skewing the calculation. Considering the data interpretation and refinement necessary prior to the Tn calculation, the Tn values for these types of aquifer must be considered as a qualitative metric.

Subsequent comparison of the Tn values with borelogs generally indicated a moderate correlation with field indications of fracture abundance or strata porosity. However, the quality of the original bore logging proved to be central to this correlation.

The data interrogation proved to be a valuable additional source of data to infer variability in LNAPL recoverability and aquifer properties such as permeability, fracture or pore connectivity, and LNAPL saturation. In this regard, the data critique provided an essential additional line of evidence for assessing remediation technique applicability within sub-areas of the plume. This was particularly valuable when evaluating the efficacy of hydraulic LNAPL removal techniques and/or practicality of staggered remediation approaches.

Furthermore, by using this data, practical efficiencies were achieved in implementation through targeted selection of LNAPL recovery techniques suited to the apparent recovery profiles in each sub-zone within the plume. Considering the variability in LNAPL recoverability and accessibility, this data enabled an evidence-based rationale on a well by well basis for optimised LNAPL recovery and justifying the progression of a tiered LNAPL remediation strategy.

CONCLUSIONS

Overall, whilst the API Tn values are considered qualitative for such dual porosity aquifers, a rigorous analysis of the LNAPL recharge data provided valuable resolution on LNAPL recoverability. The analysis provided evidence to characterise aquifer variability and assist decision making for remediation technology selection.

BIOSPARGE REMEDIATION OF LNAPL AND DISSOLVED PHASE PETROLEUM IMPACTS ADJACENT TO COMMERCIAL BUILDINGS

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INTRODUCTION

Remediation of petroleum impacted groundwater across a 1.3 hectare area has been implemented through biosparging across a network of 67 injection wells. Sparging of light non aqueous phase liquid (LNAPL) and dissolved phase hydrocarbons has occurred in open space areas and adjacent to commercial buildings. Whilst remediation has achieved a reduction of groundwater hydrocarbon impacts, monitoring of off-gas vapour generation in soil gas, sub slab and indoor air has been performed to support demonstration of attenuation of impacts within the vadose zone and no unacceptable impact to building occupants.

METHODS

Conceptual Model

An underground storage tank (UST) leak resulted in a LNAPL and dissolved phase hydrocarbon plume stretching across an area of approximately 250 metres by 50 metres at an operating manufacturing facility. LNAPL analysis reported a degraded petroleum, with LNAPL reported at the down-hydraulic gradient site boundary some 250 metres from the source zone. The unconfined sedimentary aquifer comprises sand, clayey sand, sandy clay, gravel, quartzite and/or sandy limestone materials. Discontinuous weathered limestone bands have been assessed to provide potential preferential pathways within the saturated zone. Groundwater is approximately 9 metres below ground level (mBGL) with a groundwater velocity of between 1 to 20 m/year. Commercially occupied buildings are located within the source zone and on the southern boundary of the plume. The southern boundary buildings are slab on grade construction in the vicinity of groundwater impacts.

Remedial approach

A biosparge trial was performed to prove concept and obtain design data. As a preliminary stage, a 9 injection well biosparge system was installed at the down-hydraulic gradient site boundary in January 2009. In September 2012 the biosparge approach was expanded to a further 3 wells on the boundary system and 55 wells across the down-gradient source area, in the vicinity of commercially occupied buildings. Biosparging operates 6 days per week cycled setting of 30 minutes on, 30 minutes off, injecting air at 15 litres per minute (L/min) at 40 to 60 kilopascal (kPa). Source area remediation (vicinity of the former UST) also employs soil vapour extraction to remediate vadose zone impacts.

Vapour monitoring

Three lines of evidence were utilised to assess vapour generation and impact to commercial receptors during initial operation of the 55 well biosparge system:

a) Soil gas monitoring at implant depths of 4 mBGL and 8 mBGL.
b) Sub-slab vapour pins installed at four locations within the commercial building.
c) Indoor passive air sampling over a 24 hour period.

Analysis was performed for total petroleum hydrocarbons in the C_5 to C_{12} range (speciated TPH), benzene, toluene, ethyl-benzene, total xylenes and naphthalene (BTEXN). During different stages of monitoring, biosparge system operational settings were adjusted to assess the impact of operation to vapour generation.

RESULTS AND DISCUSSION

Biosparging

Monitoring of boundary biosparge system performance at well MB33 (located 6 metres from injection wells) indicated no apparent LNAPL thickness after 17 months and a continuing trend of reduction of dissolved phase impacts towards adopted investigation levels. Monitoring of offsite well MB34 (40 m down hydraulic gradient) reported decreasing benzene concentrations.

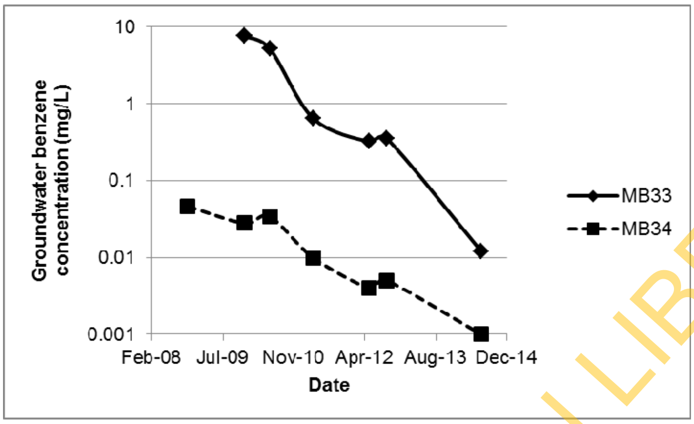

Figure 1. Benzene concentration trends.

Vapour monitoring

Biosparging operations near well MB40 (July 2014 benzene concentration of 24.1 milligrams per litre (mg/L)) resulted in increased soil vapour concentrations (SG2 at 4mBGL) above adopted the Health Screening Level (HSL). Sub-slab vapour monitoring and indoor passive air sampling indicated that benzene concentrations (with the same biosparge operational parameters) attenuated over the vertical profile of the vadose zone.

Table 1. Benzene vapour concentrations with depth during biosparge operations.

Sample Location	Sample depth (m)	Biosparge setting	Benzene (µg/m^3)
RS856	Inside building (+1)	Cycle	< 9
SS02	Beneath slab (-0.3)	Cycle	< 5
SG2S	Soil gas bore (-4.0)	Off	< 4
		Cycle	800
SG4S	Soil gas bore (-4.0)	Off	< 5
SG4D	Soil gas bore (-7.5)	Off	1 400

CONCLUSIONS

Whilst effective remediation of LNAPL and dissolved phase hydrocarbon impacted groundwater is occurring at the site via biosparging, assessment of vapour impacts in the vadose zone, beneath building slabs and within occupied spaces of a commercial building demonstrate that attenuation of hydrocarbon impacts is occurring in the vertical profile.

REFERENCES

Johnston, C.D., Woodbury, R., Bastow, T.P. and Geste, Y., 2010. Biosparging successfully limited fugitive VOCs while remediating residual weathered gasoline in a shallow sand aquifer. Proc. 7th International Groundwater Quality Conference held in Zurich, Switzerland, 13–18 June 2010), paper TU-15.

Wallis, C., Ellis, G., Medd, J., 2013. Multi-Technology Program to Remediate a laterally Extensive Hydrocarbon Plume Within a Sedimentary Aquifer, Victoria. Proceedings of the CleanUp 2013 5th International Contaminated Site Remediation Conference held in Melbourne, Victoria

REMEDIATION IN THE YEAR 2025:
HOW CLEANUP AT DNAPL SITES MIGHT EVOLVE

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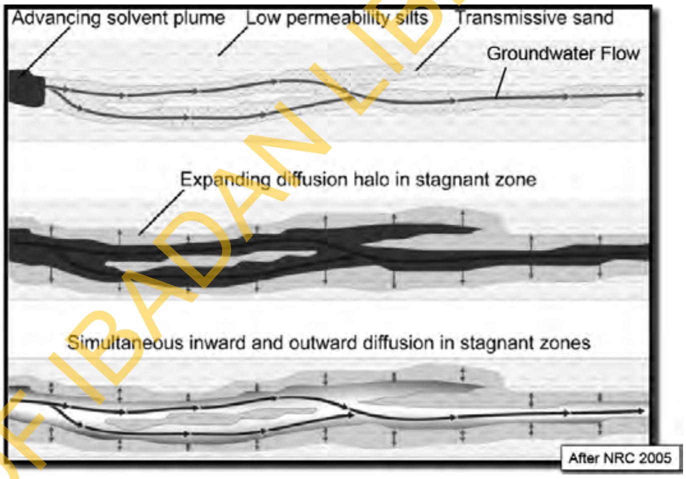
The groundwater remediation field has changed significantly over the past 30 years, with several dramatic "paradigm shifts" that reshaped the fundamental thinking about how we remediate contaminated groundwater sites. In the DNAPL-chlorinated solvents world, there have been two main periods when the prevailing conceptual model was disrupted and replaced by a new way of thinking:

- *Early 1990s: "There is something else down there" and the DNAPL Paradigm*
- *Now: "Revenge of the Geologists" and the emergence of matrix diffusion*

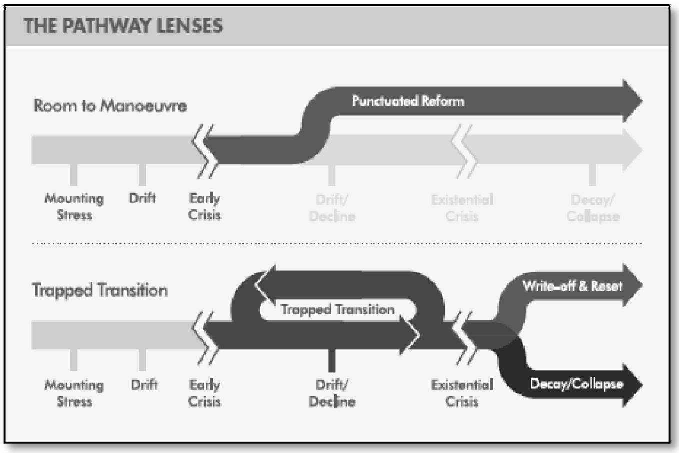
Core containing DNAPL (GSI)



Conceptual Model for Matrix Diffusion

This talk will tell a story of one person's perspective on how the DNAPL remediation field in the United States evolved over time, with an emphasis on relatively rapid changes in the underlying way people think about sites and the accompanying changes in the way that remediation is performed. Then, based on this rich history of our field, a cautious forecast of the future of site remediation will be made to the year 2025. To do this, a short summary of forecasting techniques in other fields such as business and geopolitics will be presented, such as:

- Shell's **Scenario Analysis** where they present an "array of plausible futures…of how the future will unfold." Shell's current scenarios are "*Room to Maneuver*" (where financial, social, political or technological capital encourages early action and result in effect change/reform vs. "*Trapped Transition*" (where these factors proved inadequate to withstand stresses and ultimately a reset or collapse occurs) (Shell, 2013).



- The University of Pennsylvania's **Good Judgment Project** (of which the author is a participant) where researchers devised an on-line tournament system to evaluate over 150,000 geopolitical forecasts over a two year period, and with these data developed this profile of the best geopolitical forecasters: "*they were better at inductive reasoning, pattern detection, cognitive flexibility, and open-mindedness*" (Mellers et al., 2015). An example question from the tournament is shown to the right.

Show only: Recently created

You are up $1.40 in this question.

1491 - How many countries will **officially submit a claim to the North Pole to the United Nations **between 14 January and 9 June 2015?

MOST ACTIVE ANSWER
None

88.22% chance
no change ($0.00) today

211 Predictions | 15 Comments | 45 Participants | Ends: June 09, 2015 @ 01:59am CDT

The forecast will be presented in the spirit of telling a potential story about what we in the remediation field may be doing in the next 10 years and will include:

- Speculation on future paradigm shifts that could dramatically change remediation;
- A simple application of Scenario Analysis and Good Judgment Project concepts to forecasting the future of remediation;
- Analysis of potential technological, social, and business model changes that could impact our field.

Numerous alternate outcomes will be discussed, all with acknowledgement of the uncertainty that accompanies any long-range forecast into the fog of the distant future.

REFERENCES

Mellers, B. et al. (2015) The Psychology of Intelligence Analysis: Drivers of Prediction Accuracy in World Politics. *Journal of Exp. Psychology: Applied*. Vol. 21, No. 1.

Shell (2013) *New Lens Scenarios: A Shift in Perspective for a World In Transition.*

COMBINING IN SITU THERMAL WITH BIOTIC AND ABIOTIC REDUCTION FOR DNAPL TREATMENT: PERFORMANCE AND DESIGN CONSIDERATIONS

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INTRODUCTION

Lands contaminated with chlorinated solvent dense nonaqueous phase liquids (DNAPLs) in groundwater are some of the most difficult to restore due to site complexity including, heterogeneous DNAPL distribution, multi-phase chemical transport, back diffusion, and variability in chemical mixture and properties. As such, it is becoming widely accepted that use of multi-technology treatment strategies is often required to achieve clean-up standards and significant advances have been made in how to integrate technologies effectively. Two relatively mature technologies, including enhanced in situ biotic and abiotic reduction (ISR), and thermal treatment, have been demonstrated independently for DNAPL source zones. ISR has been demonstrated to effectively treat groundwater contamination, but the effectiveness for DNAPL treatment is limited because the chemicals are only available for degradation once they are dissolved limiting the treatment rate to the order of years to decades. Thermal treatment is a proven aggressive technology for rapidly removing large quantities of DNAPL through heating, volatilization and extraction. High capitol and maintenance costs and the requirement for vapour control and secondary waste treatment, however, make this technology infeasible at many contaminated sites. ISR and thermal treatment can be combined effectively. In one application, low-energy heating is used to moderately raise *in situ* temperatures (i.e. to target 40-60˚C instead of 100˚C), which increases chemical dissolution and desorption rates to groundwater and increases contaminant availability and kinetic degradation rates. The combined effect results in increased treatment rates by a factor of 8 to 20. The low-energy heating/ISR system has a 50 to 75% lower capital equipment and operating cost compared to standard thermal by eliminating vapour and steam recovery and above ground treatment. Innovations in the state of the practice and lessons learned from Sites which have successfully implemented combined treatment strategies have resulted in a better technical and logistical understanding of important performance and design considerations.

PERFORMANCE AND DESIGN CONSIDERATIONS

An overview of the state of the art including the latest developments in ISR and thermal technologies and tools available to practitioners will be described. First, performance, and cost benefit, of the combined strategy is dependent on several factors including:

- Ability to successfully deliver amendments *in situ*,
- Ability to use available heating technologies (i.e. thermal conduction and/or electrical resistance heating),
- Hydraulic conditions that allow for propagation and retention of heat to target treatment zones,
- Sufficient treatment volume to allow for degradation reactions to come to completion before groundwater moves to a receptor,
- Sufficient vadose zone to treat contaminants that may volatilize during treatment to ensure vapour intrusion does not become an issue,
- Mass and architecture of DNAPL within the subsurface.

Technology design scenarios for using the combined thermal/ISR approach can include:

- Low-energy thermal/ISR as a stand-alone technology,
- Low-energy thermal/ISR to reduce the footprint and/or the duration of high-temperature thermal,
- Low- energy thermal/ISR for targeted heating of hotspots to enhance ISR treatment and reduce the remedial timeframe.

CASE STUDIES

Two case studies will be presented that exemplify the design elements and performance of the combined technology. A field test was conducted to demonstrate the impact of low-energy ERH with in situ bioremediation (i.e., 30-45˚C) and zero valent iron (ZVI) reduction (target 40-50˚C) to accelerate treatment of DNAPL in Ft. Lewis, Washington, USA. Heating increased contaminant dissolution resulting in contaminant mass discharge of approximately 4-8 times greater at 45˚C compared to 10˚C in groundwater. Concomitantly, this increased contaminant loading was observed primarily as reductive daughter products suggesting that degradation rates were sufficiently high to treat this mobilized mass. This equated to a treatment rate increase from approximately 175 grams (g) TCE treated/day to 1789 g TCE treated/day (Figure 1) for bioremediation and from 158 to 1270 g TCE treated/day for ZVI. Increased contaminant discharge to soil gas due to volatilization and discharge to downgradient locations in groundwater was also minimal during the test because of the high degradation rates. This approach demonstrated synergy between the two technologies evident with significant increases in both the kinetics and the residual TCE mass removal rates, and documented the validity of the strategy.

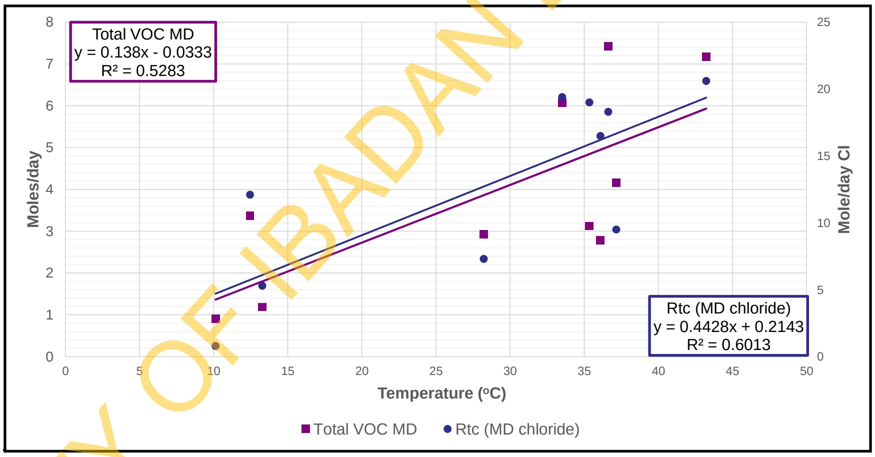

Figure 1. In Situ Degradation Rates as a Function of Temperature

An innovative multi-technology remedial strategy was implemented at Hunters Point Naval Shipyard (HPNS) in San Francisco, California, USA to treat a mixed chlorinated benzene, ethene and ethane DNAPL in groundwater. Due to the site's proximity to San Francisco Bay and the city's residents, the DNAPLs posed unacceptable risk that threatened the long-awaited transfer of an adjacent property to the city of San Francisco for redevelopment. Therefore, an expedited treatment strategy included thermal for removal of the DNAPL and ISR for polishing remaining soil and groundwater concentrations to treat the area within 18 months. High temperature thermal (i.e. 100˚C), removed highly saturated DNAPL with an 86-99.9% efficiency. However, inefficient removal of chlorinated benzenes resulted in groundwater concentrations were 1-10 ppm post-thermal. The ISR amendment emplaced prior to the thermal resulted in efficient polishing, with a >99.99% reduction in chlorinated ethene/ethane and a >86% reduction in chlorinated benzenes achieved within 900 days of thermal with a factor of 2-4 increase in the degradation kinetic rates during the period of elevated temperatures during the cooling period. The innovative approach provided cost-effective, successful clean-up within an aggressive timeframe, ultimately allowing the city's long-awaited redevelopment plans to move forward.

IN SITU SMOLDERING COMBUSTION (STAR) PRE-DESIGN EVALUATION (PDE) FOR L&DNAPL COAL TAR IN AN AQUIFER

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INTRODUCTION

Self-sustaining Treatment for Active Remediation (STAR) is an innovative, patented and patent pending thermal technology based on the principles of smoldering combustion, where the contaminants are the source of fuel. The process is self-sustaining following a short duration, low energy ignition event, such that the energy of the reacting contaminants is used to pre-heat and initiate combustion of contaminants in the adjacent area, propagating a combustion front through the contaminated zone, provided a sufficient flux of air is supplied. The porous media is key to maintaining the STAR reaction as it helps hold and recycle the released energy.

Proposed redevelopment plans at the location of a former manufactured gas plant (MGP) in northern Michigan have accelerated the timeline for full-scale cleanup. The site is impacted with MGP Dense Non Aqueous Phase Liquid (DNAPL) and Light Non Aqueous Phase Liquid (LNAPL) over approximately 0.32 hectares within a sandy aquifer. The DNAPL extends to approximately 12 meters below grade (m bg) with the LNAPL located just below the water table located at 8.5 m bg.

METHODS

A STAR PDE involving a four-well ignition/air injection system targeting both the LNAPL and DNAPL zones (two wells per zone) was conducted to evaluate key full-scale design parameters such Radius of Influence (ROI), combustion front propagation rate, and volatile mass loading. The PDE was instrumented with thermocouples to track subsurface temperatures, and covered with a cap with a vapour collection system. The captured subsurface vapour were directed to a continuous emission monitoring system to detect and quantify the combustion gases, carbon dioxide (CO_2), carbon monoxide (CO), and oxygen O_2.

RESULTS AND DISCUSSION

Self-sustaining smouldering combustion was achieved in both the LNAPL and DNAPL zones. The data presented was collected during the second of two combustion events in the LNAPL zone. During this test, combustion was maintained in a self-sustaining manner until the ROI was reached. The ROI was governed by site specific parameters (e.g., permeability) and the equipment sizing selected for the PDE.

The total petroleum hydrocarbon (TPH) concentration in the pre and post PDE soil cores indicated that on average greater than 95% of the DNAPL (average pre treatment concentration of 45,850 mg/Kg) and LNAPL (average pre treatment concentration of 13,500 mg/Kg) was removed, up to 2.6 m from the ignitions points.

CONCLUSIONS

The PDE showed that STAR can treat the LNAPL/DNAPL layers of coal tar beneath the watertable, and achieve a ROI of 2.6 m, with a propagation rate of approximately 0.36 m/day. This design information is being used to develop a full scale STAR treatment of the site.

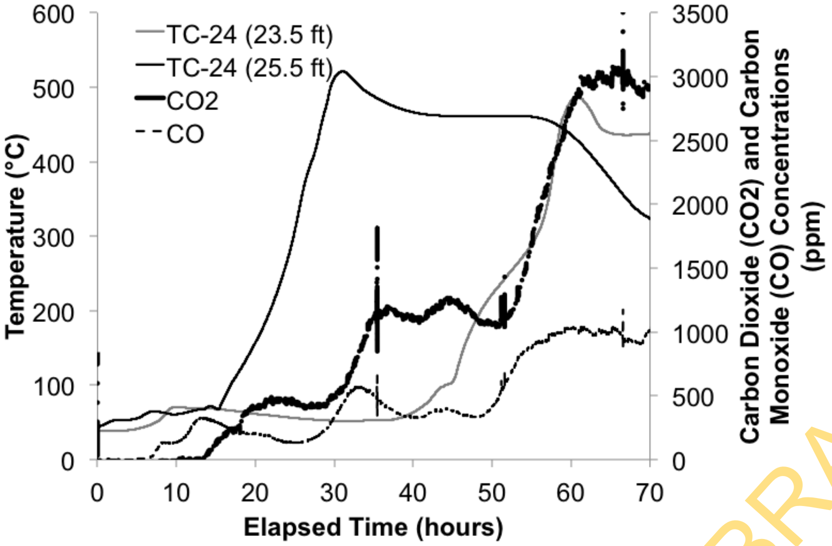

Fig.1. Combustion gas and subsurface temperature data. Onset of combustion was evident from increasing carbon monoxide and dioxide concentrations approximately 4.5 hours after preheating. Coal tar ignites approximately at 300°C which was measured in a thermocouple (TC-24) located approximately 2 feet (0.61 m) west of the ignition point, and at 7.2 m (23.5 feet [ft]) and 7.8 m (25.5 ft) bg.

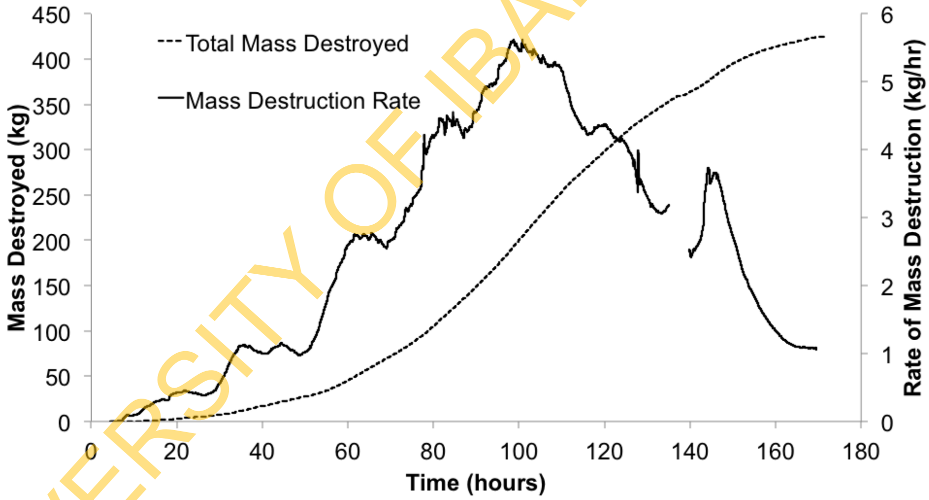

Fig. 2. Estimated coal tar mass destruction rate and cumulative mass destroyed. Mass was calculated using carbon monoxide and carbon dioxide concentration data as measured in the collected emissions. Over the 7.2 day duration of the test, an estimated total of 425 kg of coal tar was destroyed, providing an average mass destruction rate of 60 kg/day or 2.5 kg/hr.

A WEIGHT OF EVIDENCE APPROACH TO *IN-SITU* BIOREMEDIATION OF GROUNDWATER IN DNAPL SOURCE ZONES

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INTRODUCTION

AECOM installed and operated two enhanced *in-situ* bioremediation (EISB) systems between 2012 and 2015 to address chlorinated ethene impacts in groundwater. The EISB systems were designed to remediate dissolved phase concentrations of tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC) at an industrial dry cleaning facility (Lawrence Dry Cleaners) and adjacent properties located in Waterloo, NSW, Australia. As part of a Management Order issued by the NSW Land and Environment Court, AECOM was required to technically evaluate remediation and monitoring data forming multiple lines of evidence and compare remediation progress against site specific remediation criteria and strict timelines.

METHODS

Using a number of relevant guidance documents, AECOM developed an adaptable performance monitoring program to evaluate the effectiveness of EISB and to optimise remediation activities. The performance monitoring program included the use of different analytical protocols, monitoring locations, and monitoring frequencies that were systematically refined as remediation progressed. A multiple lines of evidence approach was used to demonstrate compliance (permanent reduction of contaminant concentrations) with the MO.

The lines of evidence included:

(a) Primary Lines of Evidence
    (i) Reduction in concentrations of contaminants of concern (PCE, TCE, DCE, VC).
    (ii) Reduction in size and magnitude of contaminant plume.
    (iii) Appearance of daughter products and end products of degradation (chloride and dissolved hydrocarbon gases: methane, ethane, ethene).
(b) Secondary Lines of Evidence
    (i) Changes in groundwater geochemistry (nitrate, iron, and sulfate).
    (ii) Substrate distribution (volatile fatty acids).
    (iii) Molecular Biological Tools (MBTs including *Dehalococcoides* [DHC] enumeration).
    (iv) Contaminant degradation via Compound Specific Isotope Analysis (CSIA).
    (v) Source depletion via attenuation rate modelling.
    (vi) Reduction in mass flux estimates.

RESULTS AND DISCUSSION

Primary and secondary lines of evidence were monitored throughout the performance monitoring period. In Source Area 1, where EISB was first trialled in 2009, concentrations of Significant Contaminants (defined in the MO as the sum of PCE, TCE, DCE, and VC) have reduced from baseline concentrations approaching solubility limits (~200 mg/L) to levels near detection limits (<0.1 mg/L) by 2014. As shown in Fig. 1, the dissolved phase concentrations of Significant Contaminants fluctuated as dense non-aqueous phase liquid (DNAPL) dissolution and desorption took place over time; however, the overall decreasing trend in concentrations during this time was clearly evident. Other primary lines of evidence including the generation of ethane, ethene, methane and chloride (in conjunction with decreasing

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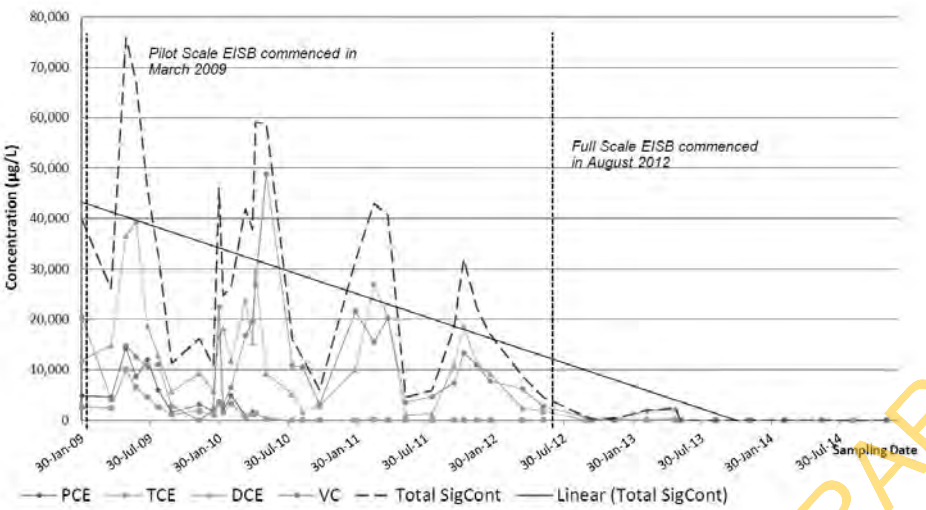
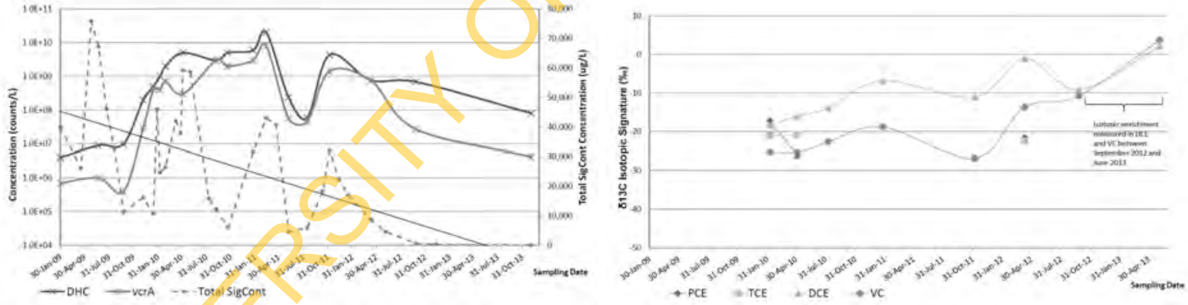


Fig. 1. Primary Line of Evidence - total Significant Contaminants in Source Area 1 (MW44).

concentrations of chlorinated ethenes) were used to infer the occurrence of anaerobic dechlorination processes.

Secondary lines of evidence were used to correlate the performance of the EISB approach with depleted concentrations of nitrate, sulfate, and ferrous iron used to confirm that the groundwater environment was sufficiently reducing for anaerobic dechlorination to occur. Substrate distribution data were used to optimise the dosing and delivery of the electron donor. MBTs provided strong evidence of increasing DHC populations during the degradation and solubilisation processes with populations tailing off following the virtually complete dechlorination process. CSIA results demonstrated isotopic enrichment directly attributed to biological degradation.



Figs. 2 & 3. Secondary Lines of Evidence – DHC populations and CSIA results at MW44.

CONCLUSIONS

Primary and secondary lines of evidence have been used to systematically demonstrate biological degradation of chlorinated ethenes based on a weight of evidence approach. The long-term results at this site represent one of the few examples of successful and validated applications of EISB on DNAPL source areas worldwide.

REFERENCES

Air Force Center for Environmental Excellence (2004). Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents, Final. Ref: 022/738863/28. August 2004.

Interstate Technology & Regulatory Council (2008). In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones. Washington, D.C.: Interstate Technology & Regulatory Council, Bioremediation of DNAPLs Team. June 2008.

RECENT DEVELOPMENTS FOR ASSESSMENT AND MANAGEMENT OF SOIL VAPOUR INTRUSION

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INTRODUCTION

Two decades of data collection ranging from large database studies to intensively monitored buildings have improved our understanding of the conceptual site model for the vapour intrusion pathway and appropriate strategies for investigation and management. Lessons learned from site data, the challenges arising from pathway complexity and variability, and new approaches and tools for more effective vapour intrusion investigations are described.

LARGE DATABASE STUDIES

Large database studies completed by U.S. EPA and Health Canada, consisting of analysis of paired, near concurrent measurements of indoor and subsurface chlorinated solvent concentrations indicate a limited correlation between subsurface and indoor air concentrations. Removing the influence of background and to account for source strength (100X background), the correlation improves with the groundwater-to-indoor air attenuation factors ranging from 2.4E-5 (25th %ile) to 2.2E-4 (75th %ile) (U.S. EPA, 2012). The attenuation factors for coarse-grained soil are approximately one order of magnitude less than for fine-grained soil (Golder, 2012), but there is less difference in attenuation factors for residential and commercial buildings, although commercial building data are relatively limited.

A U.S. EPA comprehensive database was developed for petroleum hydrocarbon compounds with the key metric the observed distance from a source for attenuation of soil vapour concentrations to below a threshold of concern. This analysis, which showed consistent attenuation due to aerobic biodegradation, led to vertical pathway exclusion distances, recommended in ITRC (2014) guidance, as 5 ft for a dissolved petroleum source and 15 ft for a LNAPL source.

INTENSIVELY MONITORED SITES

The lack of success in an attenuation factor approach, in part, led to U.S. EPA and U.S. DOD research on intensively monitored sites to better understand factors affecting primarily chlorinated solvent vapour intrusion. The research showed greater spatial variability in soil vapour concentrations was generally observed with increased distance from sources. Some site data indicated very little concentration attenuation between source and subslab sampling locations as most attenuation was across the building envelope and due to mixing in the building. Subslab vapour data, therefore, can be a poor predictor of indoor air concentrations given dynamic processes for soil gas advection and variability in peri-foundational conditions. Temporal variability in indoor air concentrations is observed on diurnal to seasonal timescales and a positive correlation between vapour intrusion and building depressurization or winter time (cold). The magnitude of the temporal variability in indoor air vapour concentrations generally ranges from one to three orders of magnitude; the high end of this variability range was observed at a site where there was significant vapour transport through a sewer. Estimates of VOC mass flux are shown to be much less variable than indoor air concentrations and potentially a useful metric for characterizing longer-term exposures. In the context of potential acute short-term health concerns associated with TCE exposures, the implications for sampling programs arising from the observed variability in indoor concentrations at intensively monitored sites is discussed. The application of these data to sites in warmer climates is also discussed.

VAPOUR INTRUSION DIAGNOSIS APPROACH

Groundwater screening criteria for chlorinated solvents are often exceeded necessitating further assessment. The variability observed has led to debate on possible approaches (Table 1), which potentially include the following strategies 1) a bottom-up approach starting with deep soil vapour characterization, followed by subslab vapour and indoor air, as warranted; 2) a multiple lines-of-evidence approach involving typically concurrent measurement of indoor air, outdoor air and soil vapour samples and other complementary data, and 3) a top-down approach where the focus is indoor air monitoring, which may employ real-time field GC/MS testing combined with diagnostic tools such as testing of pathways and pressure-control tests, when warranted.

In recent years, the tool box of methods has expanded, including highly sensitive field GC/MS to enable cost effective intensive and real-time monitoring, pressure monitoring, pressure-control tests (testing of indoor air under fan-induced positive and negative pressures), radon testing (as a tracer) and carbon stable isotope analysis (for background source assessment). A case study where selected tools were used to effectively assess trichloroethylene exposures is described. The right combination of the above approaches and tools to achieve health protective and efficient outcomes as informed by the conceptual site model and site-specific objectives has been described as vapour intrusion diagnosis (Johnson, 2015).

Table 1. Overview of Detailed Assessment Approaches for Chlorinated Solvent Vapour Intrusion.

Approach	Method	Advantages	Disadvantages
Bottom-Up	Deep soil vapour followed by subslab vapour and indoor air as warranted	When geologic barrier or fresh water lens, soil vapour data may screen out pathway	Less direct and potentially longer timelines than other methods, high spatial variability in soil vapour
Multiple Lines of Evidence	Concurrent indoor air/ outdoor air/soil vapour measurements and other complementary data	Can be useful to distinguish background from vapour sources; potentially greater confidence if different data yield similar outcomes	Lines of evidence may be inconclusive, some data may not be warranted
Top-Down	Primarily indoor air data, often relatively intensive, can include pathways (utilities) and pressure-control tests	More direct, potentially able to determine pathway signi-ficance faster and more effectively than other methods	Less complete understanding of subsurface conditions, some tools still under development

RISK MANAGEMENT

Technology borrowed from the radon industry has been demonstrated to typically be effective for mitigation of chemical vapour intrusion at existing buildings. For larger buildings, a recent development is use of mass flux as an alternate metric to depressurization with the aim of system optimization and improved sustainability. For new buildings at impacted sites, the potential options include different types of barriers (or no barrier), use of aerated floors for more efficient subslab venting, and active to semi-passive (wind turbine) venting systems. Recent site data are shown that demonstrate that wind turbines or small fans can provide for effective and sustainable means of venting or subslab depressurization. One practical consideration for semi-passive or passive systems is how to demonstrate mitigation effectiveness given the potential for confounding effects from background and cost of follow-up indoor air monitoring programs. This question could potentially be addressed through modeling and focused field studies to better understand typical reduction that can be achieved through different mitigation approaches.

DESIGN, VERIFCATION AND DEVELOPMENT OF ACTIVE SOIL VAPOUR SAMPLING PORTS IN FRACTURED BASALT

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INTRODUCTION

The collection and interpretation of soil vapour data is becoming an increasingly important phase of site characterisation in relation to health risk assessments and site remediation. When the source of the vapour isn’t known, measuring the concentration of vapours incrementally in the vertical plane may provide evidence for on-site surface spills or for the migration of off-site impacted ground water.

Here we present the installation and development method, verification process and findings of a study to measure vapour concentration through fractured basalt underlying thick clays. The overall objective was to provide a line of evidence to support the belief that the source of detected chlorinated solvents in groundwater was groundwater migrating on-site from an off-site source (rather than from an on-site source).

To achieve this objective, great effort was put into the design and verification of the soil vapour bore construction to ensure sampling ports were within rock features that would be favourable to vapour migration (e.g. fractures). The design was supported using specialist borehole camera equipment to inspect the borehole. Verification of the sample ports entailed pneumatic testing (for cross-communication between sample ports) and ‘development’ prior to sampling (to ensure sampling ports were within viable rock fractures and to counter any effects of the air hammer drilling technique).

METHODS

Nested (bores at different depths within one location) soil gas bores were installed at three locations across the site. Sampling ports were positioned ~1 mbgl in fill/underlying clay and between 3 mbgl and 10 mbgl, within fractured basalt. Groundwater at the site is approximately 11 mbgl. One bore was located in the centre of the site (among site operations), the other two were located on the site boundary hydraulically up-gradient from site operations. Bores were drilled using air hammer drilling techniques to eliminate the introduction of fluids into the boreholes.

Borehole Inspection

An optical televiewer (OTV) camera system was used to inspect the boreholes. The OTV recorded a visual log of the borehole and deviations in borehole diameter using callipers, from which the depth, orientation and aperture of fractures in the basalt could be interpreted.

Pneumatic Testing

A vacuum pump was connected to each of the nested bores in turn while the differential pressure between the remaining nested bores and atmospheric air was measured. The results of which were used to evaluate cross-connection between sampling ports. Flow rates from 0.1 L/min up to 5 L/min were progressively applied with the differential pressure between other implants and atmospheric pressure monitored.

Soil Vapour Port ‘Development’

Air hammer drilling used to drill the bores introduces significant quantities of air into the vapour system which could temporarily alter the environment that we are trying to study. Once the soil vapour bores were installed, the bores were ‘developed’ to validate that the

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vapour environment was in a state of equilibrium prior to taking primary vapour samples. The bores were purged of up to 1 m^3 during which vapour samples were collected at intervals using sorbent carbon tubes..

RESULTS AND DISCUSSION

Calliper output and interpretation of fracture orientation and aperture were used to design the position of vapour ports. Borehole logs (not shown) were produced indicating implant installation depth, fracture orientation and aperture, and borehole diameter deviations (calliper output).

Pneumatic testing at a purge rate of 0.1L/min did not induce a change in differential pressure of other implants, indicating a low potential for cross communication between ports. When the flow rate was increased to 1 L/min, a change in differential pressure was observed in the shallow implant for one location, indicating that there may be a potential for cross communication at this flow rate. However, the results indicated that purge rates in the order of 0.1 L/min would be suitable for collection of the vapour samples that are not likely to be affected by cross communication.

Samples taken during development of each sampling port indicated that consistent concentrations of compounds were measured over the volume purged (Fig 1). Interpretation of these sample concentrations indicated that the system was in a state of equilibrium. This verified that it was suitable to sample the implants for actual soil vapour measurement utilising SUMMA canisters including standard quality control procedures (e.g. helium shroud leak check).

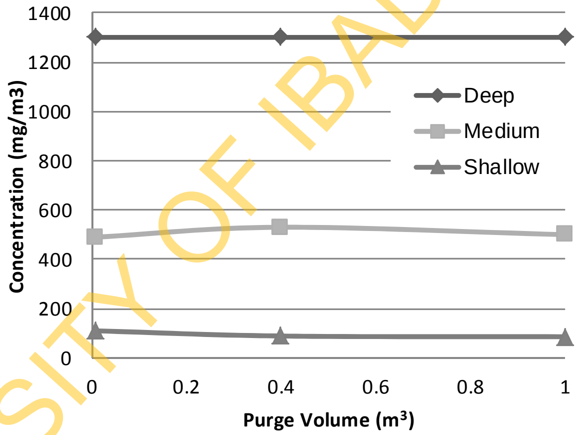

Fig. 1. Trichloroethene soil vapour concentrations in nested soil gas bore during purging

CONCLUSION

Multiple depth active soil vapour sampling ports have been used to assess vapour concentrations. A careful protocol for installation, pneumatic testing and subsequent development showed that representative vapour samples can be obtained from fractured rock with increased confidence, overcoming the confounding issues of basalt rock fracturing.

Ultimately, assessment work could be undertaken using the vapour installed in rock to better understand the vapour issues at the site and to support investigation findings.

VAPOUR (TCE) INTRUSION AND THE RELOCATION OF PEOPLE FROM THEIR HOMES — THE CAUSE, THE RELOCATION, THE SCIENCE, THE OUTRAGE

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INTRODUCTION

In Australia, and other industrialised cities, manufacturing and industry are often located close to residential properties. Clovelly Park (a southern suburb of Adelaide, South Australia) has a history of motor vehicle manufacturing, dating back to the 1950s (Chrysler). In the 1960s, widespread residential development extended to Clovelly Park - replacing the remaining farms and orchards.

In 2008, as a part of the due diligence process for the sale of its Clovelly Park site, Mitsubishi Motors Australia Limited (Mitsubishi) undertook groundwater testing at the southern boundary of its property (the Site). This testing identified the presence of elevated concentrations of trichloroethene (TCE) and other chlorinated hydrocarbons in the upper unconfined aquifer (the groundwater) at the Site.

Considerable sub-surface and indoor air testing followed and subsequently vapour intrusion was identified at buildings and homes located to the south of the Site. In April 2009, public housing residents were relocated from 16 apartments in a block of flats and three single-storey units due to elevated concentrations of TCE in indoor air. The block of flats and one unit have since been demolished.

Mitsubishi and its neighbour, Monroe/Tenneco (an automotive parts manufacturer), commissioned over sixty assessment programs. Subsequent indoor air testing at neighbouring residential properties (accept those above) were reported as having acceptable concentrations of TCE in indoor air.

BACKGROUND

In late 2013 Monroe undertook (baseline) testing inside one vacant house in preparation for a vapour intrusion mitigation trial. The indoor air concentrations for TCE in this house had previously been reported to be acceptable and below 2µg/m^3 (WHO). However, a result for one bedroom, that had not previously been tested, reported concentrations of TCE up to84µg/m^3. A second round of testing verified this result and was presented to the EPA in May 2014 (as a draft Vapour Intrusion Risk Assessment (VIRA) report).

In reviewing the draft VIRA report, it was considered that there was sufficient evidence to indicate that a public health risk existed and the need to relocate the people living in this area (31 properties) was a precautionary response to be undertaken over a 6-month timeframe.

An extraordinary meeting of the State Emergency Management Committee in South Australia took place on 25 June 2014 where it was recommended that a cross-government Taskforce be established to coordinate the Government's response to the situation outlined above.

On 2 July 2014, an unscheduled release of information relating to this matter occurred. This took place before the EPA, SA Health and Housing SA were able to speak with affected residents. The media immediately responded by converging at Clovelly Park late that evening. The manner in which this news was delivered remained the focus of considerable public and media attention in the coming days and weeks.

The residents were very distressed by the manner in which the news was delivered to them.

Considerable anger and outrage followed.

The matter was referred to the Legislative Council's Statutory Authorities Review Committee to "inquire into and report on the Environment Protection Authority's management of contamination at Clovelly Park and Mitchell Park, with particular reference to assessment and management of risks to public health by the Authority and related agencies". The Committee's inquiry is still ongoing.

METHODOLOGY

The EPA undertook a review of all available groundwater data and determined that the contamination was likely to have migrated to a broader area of Clovelly Park and Mitchell Park. The objectives of the EPA environmental assessment program were to:

- determine the nature and extent of the groundwater, soil and soil vapour contamination within an EPA Assessment Area (which encompassed industrial land and approximately 1400 mixed use properties),
- characterise the sources contributing to the soil vapour plume(s),
- prepare a human health risk assessment and a vapour intrusion risk assessment for the EPA Assessment Area,
- prepare a report for the residents in the EPA Assessment Area; and
- determine the geometry of a groundwater prohibition area including a buffer area within the EPA Assessment Area.

The environmental assessment program was commissioned in mid-August 2014. Approximately 226 drill hole locations were installed over a period of eight-weeks, including 33 groundwater wells, 171 clustered soil vapour bores (2m, 4m, 8m and 10m depths), and 25 targeted soil boreholes. Six nested vapour bores were installed inside six unoccupied slab-on-grade residential properties within the relocation area. Controlled indoor air sampling was undertaken the properties to validate the predicted indoor air modelling results. Local weather data and an ambient background air quality assessment was also undertaken.

Field sampling activities were undertaken as a 'point-in-time sampling event', completed over a three-week period, including groundwater, soil vapour, indoor air and outdoor air.

RESULTS

House-specific results were distributed to all 1400 homes in the assessment area, providing each property with a predicted indoor air concentration of TCE based on the vapour intrusion risk assessment. The EPA and SA Health developed a TCE Action Level Response Framework, which provided the EPA with a decision making tool to consistently address what further assessment work or response (if any) was necessary. 1352 properties fell within the non-detect response action level range and were considered 'safe' from vapour intrusion.

The results also identified four TCE sources of groundwater contamination on neighbouring industrial land.

The EPA commenced a targeted vapour intrusion validation environmental assessment program during early 2015. The work was completed in late June and results provided to the community in July 2015.

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The following figures provide a summary of the widespread groundwater and corresponding shallow soil vapour TCE plumes. Figure 1 identifies four contributing groundwater source areas. Figure 2 represents TCE in soil vapour at 2m below ground surface.

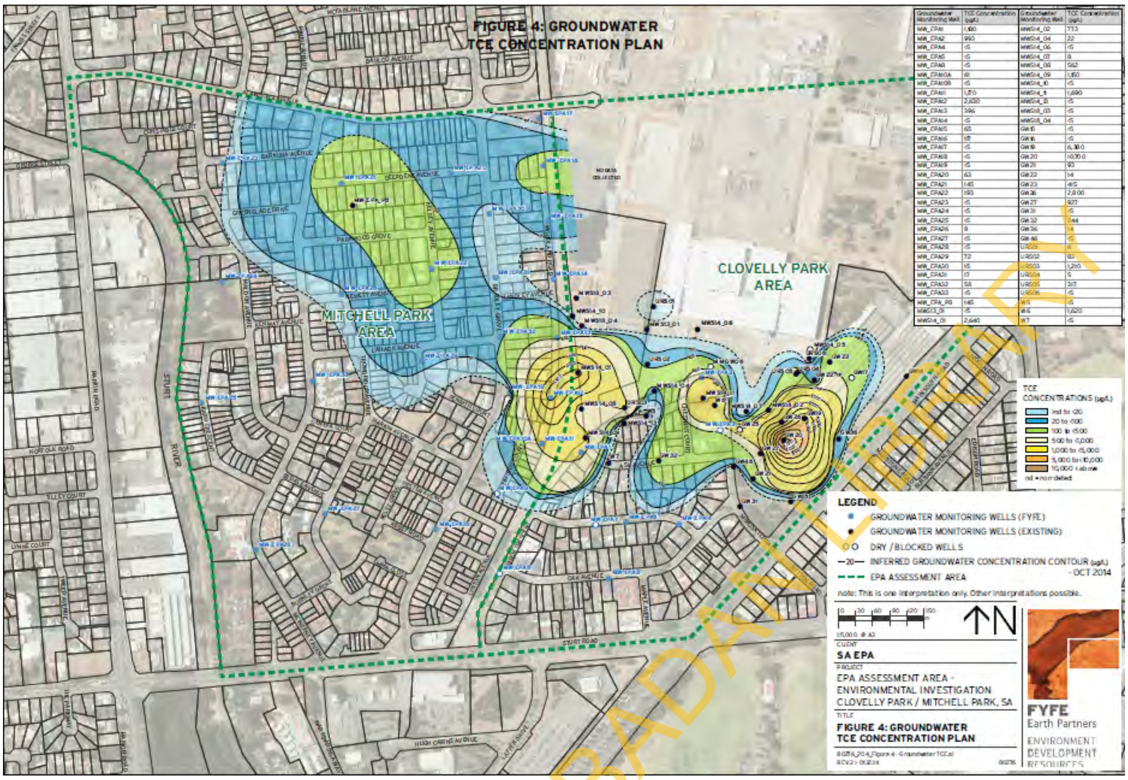

Fig. 1. Groundwater TCE concentration plume identifying four groundwater source areas on industrial land.

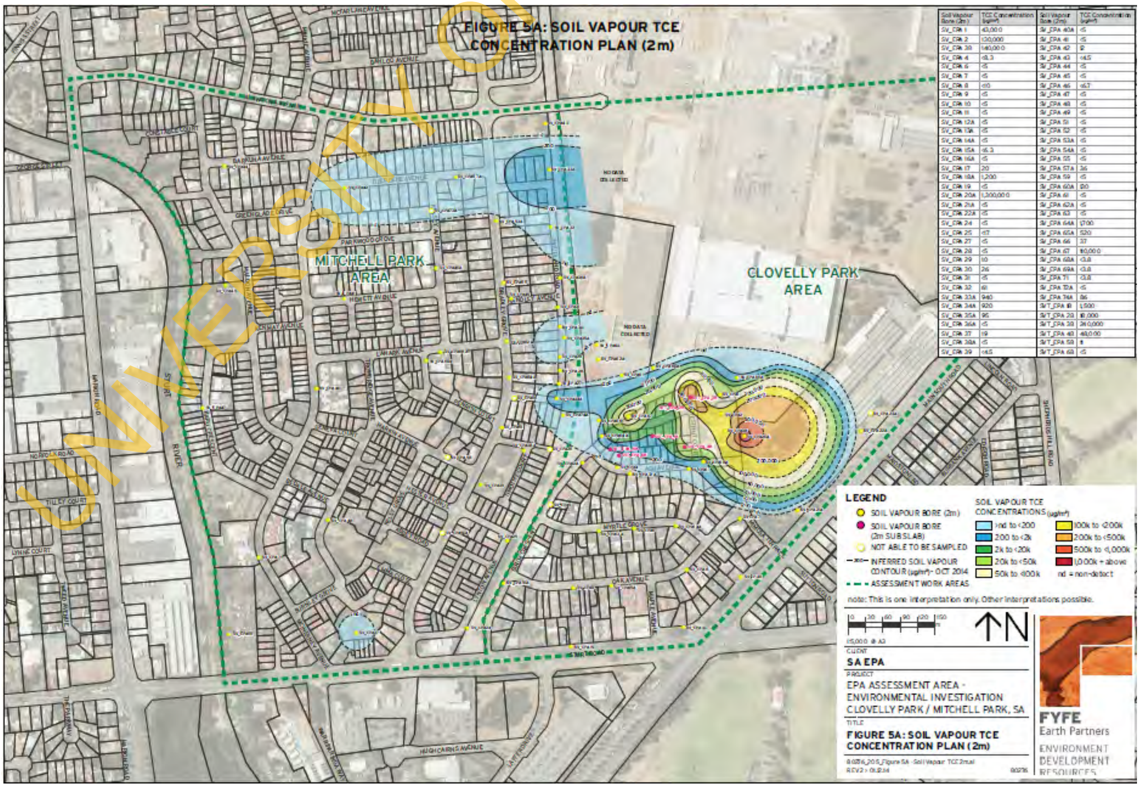

Fig. 2. TCE soil vapour concentration plume identifying elevated TCE concentrations at 2m below ground surface as 'hot spots' within residential land use.

CONCLUSIONS

The results were reported in early December 2014. Total costs for the EPA environmental assessment program were $1.5M AUD. It is the largest project of its type that has been completed by the South Australian EPA, and has been subject to considerable national and international attention.

Considerable work occurred with the community in relation to understanding what is known, what is not known and provision of the results of the environmental assessment program and outcomes. Regular update meetings and scheduled public open house sessions were held with the community.

A website for the project was established: http://cpmpproject.sa.gov.au

The report is available on the EPA website:
http://www.epa.sa.gov.au/environmental_info/site_contamination/areas_under_assessment/clovelly_park-mitchell_park

REFERENCES

Fyfe 2014, Clovelly Park/Mitchell Park Environmental Assessment, Environment Protection Authority, South Australia, Reference 05/17900, 61324, 3 December 2014.

VAPOUR INTRUSION MITIGATION USING A DRAINAGE LAYER BELOW A LARGE COMMERCIAL FLOOR SLAB

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INTRODUCTION

This paper describes an innovative design for a vapour intrusion mitigation system for a three level commercial building with a footprint of approximately 3,500 m^2 on a former industrial site in suburban Adelaide. Construction had already begun in late 2013 when, during the initial groundworks, a substantial volume of soil containing trichloroethene (TCE) was encountered. A soil gas survey was conducted to assess the magnitude and extent of the TCE distribution and the potential for health risks from vapour intrusion to indoor air. A grid of 15 shallow soil vapour wells was installed across the building footprint, mostly within the compacted and levelled construction fill that had already been prepared for the building. TCE concentrations ranged from 1,000 µg/m^3 to 1,000,000 µg/m^3 across much of the building footprint. A preliminary risk assessment concluded that the identified soil vapour impacts were likely to lead to unacceptable levels of TCE vapour intrusion into the proposed building.

Given that the construction process was already underway, remediation works were impractical and a sub-slab vapour mitigation system was added to the construction process. The building footings had already been designed, the ground works had already been completed and the construction schedule had already been determined. The building was to be constructed on a network of grade beams forming a 7m x 7m grid of closed cells beneath the ground floor slab. The fact that the construction fill had already been placed and prepared prevented the placement of a gravel venting layer as would typically be used in such a system. The design innovation consisted of laying a drainage layer below the floor and using horizontal slotted pipes to transect the grid of closed cells below the floor. This provides very uniform and highly permeable conditions below the floor with minimal loss of headroom, and allows a vacuum to be sustained below the floor with minimal electrical power, which will result in considerable savings over time.

METHODS

The sub-floor vapour mitigation system comprises a network of slotted 10 cm PVC pipes laid in 50 cm deep by 30 cm wide trenches in an east west orientation beneath the ground floor slab of the building. The slotted pipes were connected to 15 cm un-slotted PVC collector pipes running north-south along the western and eastern wall of the building. 16.5 cm stainless steel riser pipes extend upwards from each of the collector pipes near the centre of each wall to emerge on the roof of the three level building. The trenches containing the pipes were backfilled with gravel to allow free passage of air and then rolled and levelled in preparation for the slab. A drainage layer of TechDrain T7 vent mat was placed on top of the compacted soils with bidim® A14 non-woven geotextile layers above and below. Once this layer had been laid the concrete for the slab was poured directly onto the geotextile covered vent mat.

Following construction, two 120V Obar GBR76 SOE Radon fans were installed on the roof at each of the two riser pipes to depressurize and ventilate the sub-floor void. The fans were installed on the riser pipes with a transformer, gate valve and vapour exhaust stack at each location. Monitoring alarm devices (RadonAway CheckPoint 2R Mitigation System Monitor with Remote Alarm) were installed in each of the two vertical risers. The monitors are designed to activate a continuous alarm should the negative pressure in the riser fall below a pre-set threshold, indicating possible system failure.

RESULTS AND DISCUSSION

Commissioning and optimisation of the system commenced on 3 February 2015. A grid of 15 sub-slab depressurisation measuring points were established across the footprint of the building by drilling 1 cm diameter holes through the ground floor slab into the vent mat laid immediately beneath the slab. A series of sub-slab vacuum measurements were then conducted with both fans operating at full power (350 W each). The negative pressure and maximum air flow velocity in the stack just below the fan was also measured at both roof-top stacks. Under these full power operating conditions a stack emission flow velocity of approximately 20 m/s and negative stack pressures of > 500 Pa were reported. Sub-slab depressurisations of approximately 180 Pa, far in excess of the design requirement of >1 Pa, was recorded across the building.

The power to the fans was progressively reduced until the air flow velocity at the two fans was approximately 3 m/s and the negative stack pressures were approximately 30 Pa. Sub-slab vacuums were then measured at all points with both fans operating. Negative pressures in the range 8 to 23 Pa were measured, indicating more than adequate sub-slab depressurisation at this very low power setting.

Two rounds of measurements were then conducted with each fan operating on its own, leaving the other fan switched off with the stack unsealed (to mimic conditions after failure of one fan). Measureable vacuum values in the range 2 to 12 Pa were recorded at all locations with both the western and eastern fans operating individually. It was therefore concluded that the fans are capable of maintain a satisfactory sub-floor vacuum at this low power setting, either jointly or individually should one fan fail.

A series of experiments were also conducted to determine the speed of the response of the vacuum beneath the slab when the fans were switched on and off. Measurement of the changes in sub-slab pressure at measuring point near the centre of the building showed a >90% response within 30 seconds of the fans being switched off and then switched on again. This was interpreted as evidence of the efficiency of the system due to good connectivity and free flow of air beneath the slab across the footprint of the building.

Indoor air validation sampling was subsequently conducted at eight locations across the ground floor of the building. These validation samples returned concentrations of TCE and related compound below the laboratory limit of reporting at all locations.

The sub-floor vapour mitigation system was designed, installed and commissioned in parallel with the construction process in a manner that caused little or no delay to the construction schedule and consequently minimised the losses incurred by the site owner as a consequence of the TCE contamination.

CONCLUSIONS

The system is highly efficient and able to maintain a more than adequate sub-floor vacuum with a total power draw of less than 200 watts. Testing indicated that even upon failure of one of the fans, sub-floor design vacuums were maintained across the building footprint with one operational fan. Indoor air validation sampling conducted at eight locations across the ground floor of the building confirmed that the concentrations of TCE and related compound were below the laboratory limit of reporting at all locations. This design will minimize the long-term operating costs and maintain a high level of protectiveness with minimal cost.

ATTENUATION FACTORS FOR CHLORINATED VOCS — LESSONS LEARNED THROUGH 15 YEARS OF VAPOR INTRUSION EVALUATION IN EXISTING BUILDINGS

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INTRODUCTION

Volatile organic compounds (VOCs) that are spilled on the ground or released into the subsurface may migrate in the subsurface environment and eventually enter buildings as a gas or vapour by seeping through cracks in building foundations, sewer lines and other openings. This process is referred to as vapour intrusion (VI). Vapour flow from a source and into a building can be influenced by a number of factors, including contaminant characteristics, soil properties, and building related factors such as building design, foundation integrity and building depressurization due to the operation of exhaust fans or heating units within the building. Vapour concentrations generally decrease (attenuate) as they migrate along the VI pathway from source through the intervening soil between the source and a building, and particularly upon entry into a building where the soil vapour mixes with and is diluted by the existing air through the natural or mechanical ventilation of the building. The reduction in concentration is often expressed as an attenuation factor, defined as the ratio of an indoor air concentration to a subsurface vapour concentration at the time and point of measurement.

The U.S. Environmental Protection Agency (US EPA) in 2002 released VI guidance (US EPA 2002), which included regulatory VI screening levels based on generic attenuation factors developed from the limited dataset of VI pathway sampling results available at the time. US EPA continued to compile VI data and in 2012 released a report on its updated database (US EPA, 2012) that presented the distribution of empirical VI attenuation factors represented by the buildings in the database. The authors of the report used a variety of techniques to identify attenuation factors attributable to VI, removing the impact of background contributions to indoor air concentrations (Dawson and McAlary, 2009) to the extent practicable, and explored the influence of chemical type, depth to source, soil type, and building foundation type on the derived VI attenuation factors.

This paper presents a review of the key findings of US EPA's 2012 VI database report and re-evaluates the database using mass flux concepts, incorporating the lessons learned from 15 years of VI investigations at multiple sites. A case study is then used to illustrate how to develop soil and groundwater clean-up levels protective of the VI pathway based on site-specific attenuation factors derived considering mass flux concepts.

APPROACH

Mass Flux and Attenuation Factors

VOC migration in the vadose zone occurs within the soil pore spaces by diffusion and/or advection. Advection is believed to be significant only near building foundations where pressure gradients induce flow; otherwise diffusion is the controlling (and rate limiting) mechanism for mass transport from a source to the vicinity of a building (Johnson, 2005). Steady state vertical diffusive mass flux through soil can be calculated from the bulk soil concentration gradient and an effective diffusion coefficient (Figure 1). Since vapour flux through the vadose zone generally is the rate limiting step, the mass flux measured with sub-slab depressurization or building depressurization techniques also provides a measure of the available mass flux (Figure 1). The indoor air to subsurface source attenuation factor can therefore be expressed using mass flux concepts in terms related to building ventilation rates, effective diffusivity controlling vapour transport in soil, and the depth to the source.

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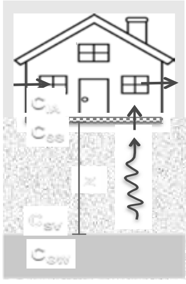
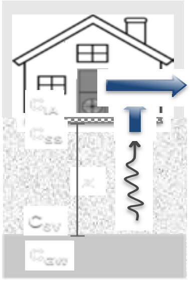
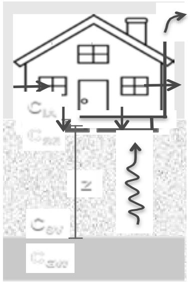


Mass flux estimation under natural conditions



Mass flux estimation under forced depressurization within the building



Mass flux estimation under forced depressurization beneath the building

Figure 1. Schematic Diagram of Mass Flux Estimation Methods.

SUMMARY AND CONCLUSIONS

Mass flux characterization is an alternative to conventional indoor air and subsurface soil vapour sampling that significantly reduces the uncertainty due to temporal and spatial variability typical of individual VI pathway sample concentrations. In combination with the current regulatory approach based on generic attenuation factors, mass flux concepts can be used to derive site-specific attenuation factors and, therefore, site-specific soil and groundwater clean-up levels that are defensible and protective of the vapour intrusion pathway. This approach provides a means of making risk management decisions with a reduced risk of false positive or false negative results (i.e., a robust decision) using fewer sampling events, which will reduce costs.

REFERENCES

Dawson, H.E. and T. McAlary (2009) A compilation of statistics for VOCs from post-1990 indoor air concentration studies in North American residences unaffected by subsurface vapor intrusion. Ground Water Monitoring and Remediation, Vol. 29, No. 1, pp. 60-69, Winter 2009.

Johnson, Paul C. (2005) Identification of Application-Specific Critical Inputs for the 1991 Johnson and Ettinger Vapor Intrusion Algorithm. Ground Water Monitoring & Remediation, Vol. 25, No.1, pp. 63-78, Winter 2005.

U.S. Environmental Protection Agency (2002) OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils. EPA 530-D-02-004. November.

U.S. Environmental Protection Agency (2012) EPA's Vapor Intrusion Database: Evaluation and Characterization of Attenuation Factors for Chlorinated Volatile Organic Compounds and Residential Buildings. EPA 530-R-10-002. March 16.

RESULTS FROM CONTINUOUS MONITORING OF CHLORINATED SOLVENT VAPORS: RAMIFICATIONS ON SOIL GAS, SUB-SLAB SOIL GAS AND INDOOR AIR SAMPLING

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INTRODUCTION

Continuous monitoring of chlorinated volatile organic compounds (TCE & PCE) has been performed at five sites over the past seven years. Three of the sites were USEPA-ORD research sites with the goals on studying temporal variations in indoor air, soil gas and sub-slab soil gas concentrations. The other two sites monitored were commercial structures with active business operations.

The results from the EPA studies have significant ramifications on soil gas sampling, sub-sub sampling and indoor air sampling strategies. The temporal studies show little variation in soil gas and sub-slab soil gas concentrations over periods as long as 100 days in the dead of winter. Indoor air variations over this same time-period were infrequent and of short duration, but did vary in concentration by 5 to 20 times. Ramifications on soil gas and indoor air sampling strategies from these data sets will be discussed, as well as ramifications on the utility of sub-slab data for assessing the vapor intrusion pathway.

The results from the three commercial sites demonstrate the potential benefits of continuously monitoring indoor air concentrations over time. At one site, the monitoring data were used to determine if shutting off an active mitigation system had any effect on the indoor air. At the second site, the monitoring data were used to determine if the indoor air PCE concentrations were from indoor sources or from the subsurface. At a third site, continuous monitoring of indoor air TCE levels has been ongoing since April 2, 2015. Data from all of these sites will be presented and discussed.

CONCLUSIONS

The ramifications from these studies on indoor air sampling, particularly regarding short-term (24-hour) exposure to trichloroethylene (TCE) will be discussed.

PETROLEUM HYDROCARBONS – OXYGEN DEMAND MODEL AND DATABASE USED TO SUPPORT SCREENING DISTANCES

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INTRODUCTION

Empirical data, comprising paired petroleum hydrocarbon soil vapour and groundwater source concentrations from sites in Australia and the United States, has been compiled, reviewed and evaluated to establish screening distances for dissolved and non-mobile light non-aqueous phase liquid (LNAPL) petroleum groundwater sources (CRC CARE 2013; Lahvis et al. 2013; USEPA 2013). A screening distance is a vertical distances between the source (including smear zone where present) and a depth in the soil profile where the hydrocarbon vapours are considered to be fully attenuated, i.e. the vapour concentrations are so low that they pose a negligible risk to human health.

The Australian database has been further reviewed to determine if the behaviour of petroleum hydrocarbon vapours observed in the data correlates with the instantaneous reaction model for hydrocarbon biodegradation (oxygen-demand model) (Davis, Patterson & Trefry 2009), and whether the combined evaluation of both the model and data provides additional supporting evidence for the screening distances.

METHODS

The attenuation of petroleum hydrocarbons from a subsurface source towards the ground surface (or a building foundation) is dominated by aerobic biodegradation processes. The potential for biodegradation to effectively attenuate hydrocarbon vapours is dependent on the source strength and the availability of oxygen in the subsurface. Modelling of the biodegradation of petroleum hydrocarbons has been undertaken using coupled oxygen-dependent first-order reaction kinetics that define an anaerobic zone, biodegradation zone and an aerobic zone. An instantaneous reaction model (Davis, Patterson & Trefry 2009), where the rate of biodegradation at the anaerobic/aerobic interface can be considered instantaneous, has been considered in this study.

The model has been considered in conjunction with empirical data available in the Australian petroleum database. The database comprises data (source and soil vapour data) from a range of sites that include dissolved phase (28% of data) and LNAPL (72% of data) located within a range of geological profiles that include fractured rock. The review undertaken has focused on data relevant to sites where LNAPL is present. This data has been reviewed in conjunction with the instantaneous reaction model (as conceptualised in **Figure 1**) to determine the depth at which the anaerobic/aerobic (instantaneous reaction) interface is present, where the measured data sits in the soil profile in relation to the model interface (i.e. if it sites above or below the interface) and whether the vapour concentrations reported in the anaerobic or aerobic zones match with the model.

The combined instantaneous reaction model and vapour data have been evaluated to determine if they support the vertical screening distances derived from review of the empirical data alone. The database has also been used to review the influence of slab size, in conjunction with the oxygen limited model used to define the size of a slab where oxygen may be present beneath the whole slab, where biodegradation can occur (Knight & Davis 2013).

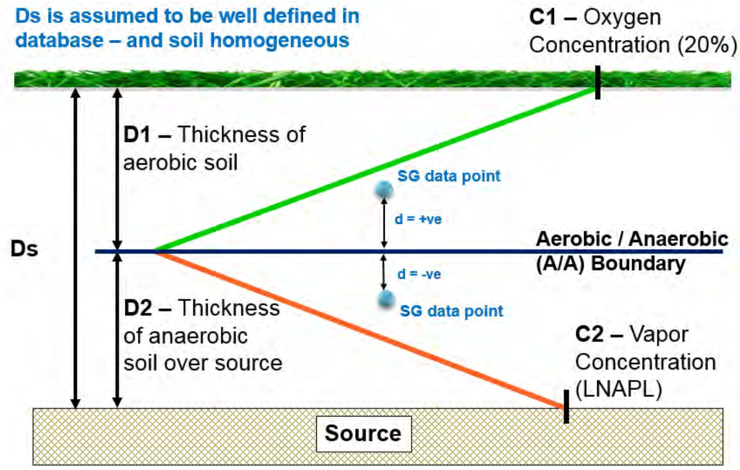

Fig. 1. Conceptualisation of Instantaneous Reaction Model and Approach to Reviewing Vapour Data Measured above LNAPL

CONCLUSIONS

The review undertaken has determined the following:

- The vapour data within the Australian database can be well explained using an (oxygen limited) instantaneous reaction model.
- The presence of a slab above LNAPL sources has the potential to affect the migration of oxygen into the subsurface, limiting biodegradation. The vapour data relevant to the presence of slabs in the Australian database can be explained using an oxygen-limited model.
- The (oxygen limited) instantaneous reaction model provides an additional line of evidence to support the screening distances defined and adopted in Australian guidance.

REFERENCES

CRC CARE 2013, *Petroleum hydrocarbon vapour intrusion: Australian Guidance*, CRC CARE Technical Report no. 23, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Davis, GB, Patterson, BM & Trefry, MG 2009, 'Evidence for Instantaneous Oxygen-Limited Biodegradation of Petroleum Hydrocarbon Vapors in the Subsurface', *Ground Water Monitoring & Remediation*, vol. 29, no. 1, pp. 126-137.

Knight, JH & Davis, GB 2013, 'A conservative vapour intrusion screening model of oxygen-limited hydrocarbon vapour biodegradation for an impervious slab building', *Environment international*, vol. (submitted).

Lahvis, MA, Hers, I, Davis, RV, Wright, J & DeVaull, GE 2013, 'Vapor Intrusion Screening at Petroleum UST Sites', *Groundwater Monitoring & Remediation*, pp. n/a-n/a.

USEPA 2013, *Evaluation of Empirical Data and Modeling Studies to Support Soil Vapor Intrusion Screening Criteria for Petroleum Hydrocarbon Compounds*, Washington, DC.

VALIDATION OF TCE & PCE IN REMEDIAL EXCAVATIONS USING VAPOUR HEADSPACE IN VIAL SAMPLING

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INTRODUCTION

Remedial excavations at a former industrial site in eastern Sydney, contaminated with tetrachloroethene (PCE) and trichloroethene (TCE), were validated using a newly developed technique whereby soil vapour headspace concentrations were analysed directly from VOC vials. Site-wide soil vapour measurements showed widespread volatile halogenated compound (VHC) concentrations in the range 100,000 to 500,000 µg/m^3 at depths of 1 m in a sand profile. Remediation of the soil consisted of excavation of the heavily impacted areas to a depth of 3 m, followed by treatment of the excavated soil in constructed vapour extraction piles. So as to allow documentation of remaining impacts at the walls and floors of the soil excavations, soil validation samples were taken using a new sampling method – vapour headspace-in-vial, developed specifically for the project.

This paper describes the new method, presents the rationale for its use, including its advantages over conventional methods and compares comparative data for conventional soil sampling and the new method.

Rationale for the development and use of a new sampling method

A traditional approach to the validation of soil excavations is to collect and analyse samples of the solid soil matrix from the floor and walls, with the total extractable mass of the contaminants then compared to applicable criteria. There are no Australian criteria for VHCs applying to soil matrix samples relevant to health risks. The National Environment Protection (Assessment of Site Contamination) Measure (2013 edition) states that there are significant limitations and uncertainties associated with the assessment of volatile organic chlorinated contaminants on the basis of soil concentrations. Commonly, the risk pathway driving health risk for VHCs is vapour intrusion. At operational or other undisturbed sites this potential vapour intrusion risk is typically assessed from field measurements of soil vapour in the existing soil profile or beneath floor or outdoor pavement slabs. However, for validation of excavations, that method is not feasible due to restricted access to excavations. Due to the impracticability of conventional soil vapour measurement methods for the purpose of validating excavation walls and floors, and because of the uncertainties in the usefulness of soil matrix samples, (*Dawson et al*., 2015) a new sampling and analysis method was developed and used as a means of quantifying soil vapour pore space concentrations in the excavation walls and floors.

METHODS

The new vapour headspace in vial sampling and analytical method described here comprised near filling a 40 mL glass vial with soil collected from a grab sample of soil from the validation point on the excavation's floor or walls. When a volume of soil is placed in a sealed vial, the vial headspace will equilibrate with the soil. At the point of equilibrium the headspace vapour concentration will equate to the pore space concentration within the soil matrix. This is a consequence of the law of molecular diffusion.

After equilibration to room temperature at the analytical laboratory a sample of headspace vapour was syringe extracted from the vial and analysed by GC-MS. The concentration of VOC vapours in the headspace of the vial forms an equilibrium with vapour concentration in the pore space of the soil within the vial and as such the method represents an alternative to sampling soil vapour in-situ.

The headspace-in-vial method is not equivalent to a standard laboratory headspace analysis. The standard headspace method involves the heating to 85 ^{o}C of a soil sample in water in a part filled VOC vial. VOC partitioned into the headspace is syringe extracted and analysed by GC-MS. Partitioning coefficients are then used to estimate the total mass of volatile compounds within the original soil sample. The modified method developed for validation of excavations is significantly different and was designed to measure contaminant concentrations as vapours in the soil pore space – not the mass of contaminant in the total sample.

Laboratory reporting limits from the directly extracted and analysed vial headspace vapours were 1,000 µg/L for both PCE and TCE. These reporting limits were sufficiently low for the objective of guiding the extent of soil excavations and determining remnant vapour intrusion risk.

RESULTS AND DISCUSSION

Twenty one co-located soil vapour headspace vial samples and soil matrix samples were collected and analysed. Comparison results are shown in Figure 1.

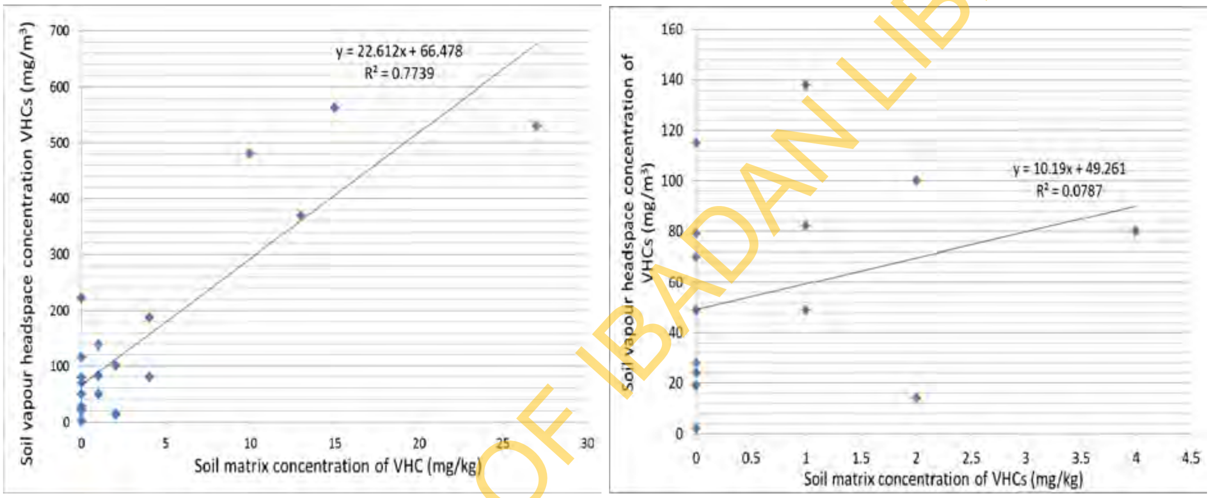

Fig. 1. Relationship between analytical results from co-located samples of soil vapour headspace (headspace-in-vial method) and conventional soil matrix sampling. Left: full range of concentrations; Right: lower concentration range

The strong correlation between the results of the two methods, $R^2 = 0.77$, indicates soil vapour is strongly dependent on VHC content of the soil, as would be expected from theoretical considerations. However, the data show that for soil vapour concentrations less than 150 mg/m^3 there is a very weak relationship ($R^2 = 0.08$). This result indicates that the soil matrix analytical detection limit of 1 mg/kg is inadequate for identifying resulting soil vapour concentrations up to about 150 mg/m^3. Vapour concentrations of less than 150 mg/m^3, for several VHCs such as PCE and TCE, can present significant health risks.

CONCLUSIONS

The new headspace-in-vial method provides a more targeted measurement of the principal risk driver at VHC contaminated sites – vapour intrusion. Although data collected using the new method correlate strongly with conventional soil sampling data in heavily impacted soil, conventional soil sampling appears to be an ineffective method at lower, though still significant, vapour concentrations.

REFERENCES

Dawson, H., Lutes, C.,Carr, D., McAlary, T. and Truesdale, R. (2015) Vapor intrusion pathway screening for soil excavation remedies. Presented at: AEHS Vapor Intrusion Workshop March 23, 2015.

CHLORINATED VAPOUR INTRUSION — COST-EFFECTIVE SCREENING & MANAGEMENT USING INDOOR RADON

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INTRODUCTION

The assessment of exposures from subsurface chemical contaminants forming vapours that intrude into the indoor air of overlying buildings (like naturally-occurring radon (Rn) does) has been particularly challenging for slowly degrading (recalcitrant) chemicals such as chlorinated solvents. Chlorinated Vapour Intrusion (CVI) involves the complex interaction of a large number of variables. After a long history of attempts to use external samples to estimate indoor concentrations (similar to that which took place for Rn decades ago) it is now clear that only samples of indoor air can fully represent the influences of all of these factors. However, the fundamental challenge for assessing CVI indoor air exposures is the effectively-unpredictable variability across space (between buildings) e.g., due to source-locations/building factors; and over time, given naturally-varying intrusion driving forces such as weather. Both challenges have been faced/addressed by Rn policies earlier. Furthermore, the CVI pathway for exposure can be as significant as the groundwater-ingestion (drinking-water) pathway and should be monitored/managed similarly for the long-term, e.g., via Monitored Natural Attenuation for as long as the source remains. Additionally, CVI exposure concerns now include health effects from only short-term (e.g., *in utero*) exposures that may need more frequent verification/monitoring. Methods for more cost-effective screening and long-term management of CVI exposure would benefit all stakeholders. This state-of-the-science review and proposal is primarily focused on residential scenarios.

METHODS

Over three decades of Rn intrusion studies and nearly two decades of chemical CVI studies, as well as their corresponding evidence-based policies, were reviewed. This included two on-going 'data-rich' CVI research houses with long periods of high-frequency indoor Rn and CVI data. The compiled Rn and CVI evidence, and evidence-based policies, were compared for similarities and differences, and evaluated under both the current 'Conventional' approach to CVI assessment, and under a hypothetical 'Ideal' approach, based on current understanding.

RESULTS AND DISCUSSION

Soil gas typically includes Rn and can include CVI-sourced vapours. The intrusion of near-building soil gas is building- and time-specific. The intrusion pathway for Rn is simpler than for CVI, e.g., has a more-constant source and decay rate and is typically from nearer the building. However, once in near-building soil gas the behavior of Rn and CVI components can be very similar. Both of the U.S. CVI-study homes, that have been sampled sufficiently to be able to observe it, have found that episodic peaks cause the majority of the exposures to occur over a small percentage (~5%) of the time. Such temporal variability can cause Conventional short-duration indoor air samples, collected at arbitrary times (relative to naturally varying conditions), unlikely to be representative of the peak-driven short- or long-term average exposures. A similar but less-dramatic effect was recognized for Rn earlier.

To address this temporal variability some CVI-workers are now recommending whole-house 'controlled [depressurization] tests' that can make short-duration samples more meaningful (Johnson 2015). While this presents distinct advantages over the Conventional limited-duration assessment under naturally-varying conditions, it is building-specific and likely to be impractical unless focused on higher-priority buildings. Conventionally, a small number buildings are selected for indoor air testing typically based on estimates of underlying source concentrations. However non-obvious building-specific features/factors can cause the indoor levels from a given source term to vary by orders of magnitude. Thus, an 'Ideal' CVI assessment would monitor all buildings, with potential for CVI, and through time, for as long as the source remains (similar to the recommendations for Rn and drinking water exposure).

Indoor Rn is easily measured, even continuously, at a low cost, allowing observations from essentially all buildings (with potential for chemical vapor intrusion) and across all time. More specifically, indoor Rn measurements can provide evidence of building-specific susceptibility to nearby soil gas intrusion, including via pipes etc., and its variability across time. When indoor Rn is >3-5 times that in outdoor air, Rn-evident soil gas intrusion is occurring and other components of near-building soil gas may also be intruding. This can be used to screen/prioritize individual buildings, and times, for more CVI-source-specific sampling.

Detailed studies also suggest that indoor Rn could be used for long-term monitoring of CVI exposure potential. Evidence from the Utah VI-study house shows visually-apparent approximately-correlated change in the behavior of both Rn & CVI vapors, i.e., the qualitative change in direction, increasing and decreasing together (under both naturally-varying and controlled (de-pressurized) house conditions). The EPA's Indy-house research team observed and statistically quantified the similarity of intrusion behavior of Rn and chemicals over a seven-month period using 1-week-long chemical samples. They found "a strong statistical relationship between increases in Rn concentration and VOC concentrations in indoor air". More specifically, they statistically characterized the Rn-CVI relationship they observed for the *change* in Rn levels measured over the last two weeks to predict the *change* in CVI levels over the same time period and found a "strong statistical relationship … statistically significant at the 1% level" [i.e., 99% confident] (U.S. EPA 2015).

CONCLUSIONS

Decades of evidence including some of the most recent research indicates that naturally-occurring Rn in indoor air presents an opportunity for cost-effective screening/prioritization and possible long-term management of CVI concerns, across both space (buildings) and time. Buildings with elevated Rn levels (relative to outdoors), and times (with more-elevated levels) can be 'screened-in' as having Rn-evident-susceptibility/priority for soil gas intrusion, and elevated-potential for CVI concerns, or not. These screening methods can supplement or replace some amount of chemical-sampling under either Conventional naturally-varying or controlled intrusion conditions, by prioritizing these more 'expensive' efforts on buildings, and times, with clear (Rn) evidence of soil gas intrusion. Furthermore, it may be possible to use indoor Rn for the long-term (& cost-effective) management of CVI potential/concerns for those buildings overlying sufficiently-elevated levels of Rn in soil gas, but continue to have 'low' indoor Rn levels (under either natural or controlled conditions). The use of indoor Rn as an indicator of building-specific susceptibility to CVI exposures can present cost savings and other benefits for all CVI stakeholders.

REFERENCES

Johnson P.C. (2015), *Diagnosing vapor intrusion occurrence, impact, and contributing pathways*. Presented at the EPA-AEHS VI-Workshop, San Diego, CA, March 23 https://iavi.rti.org/WorkshopsAndConferences.cfm?PageID=documentDetails&AttachID=824

U.S. EPA (2015), *Simple, Efficient, and Rapid Methods to Determine the Potential for Vapor Intrusion into the Home: Temporal Trends, Vapor Intrusion Forecasting, Sampling Strategies, and Contaminant Migration Routes*. EPA/600/R-14/397. Office of Research and Development, National Exposure Research Laboratory. Las Vegas, NV.

COMMUNITIES AND VAPOUR INTRUSION

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INTRODUCTION

For more than a dozen years, environmental regulatory agencies within the United States have been leading hundreds of vapour intrusion investigations. Vapour intrusion describes the pathway through which volatile subsurface contamination migrates into overlying buildings. While impacted communities have an interest is all environmental responses in their midst, their role is particularly significant at vapour intrusion sites because by definition in involves indoor air. Thus, the cooperation of the people who live, work, study, worship, or play within potentially affected structures is essential to the success of the environmental response.

The author has visited dozens of vapour intrusion sites within the U.S, providing technical assistance, leading workshops, and meeting not only with the public but also with regulators, the regulated, the media, and local officials.

See http://www.cpeo.org/brownfields/brown.html#vapor

BACKGROUND

Vapour intrusion refers to the migration of toxic vapours from the subsurface—that is, soil or groundwater—into homes, schools, and other overlying buildings. Though many substances, such as petroleum hydrocarbons and even elemental mercury, can intrude into buildings, sites that require a response usually contain chlorinated solvents—that is, volatile organic compounds (VOCs) such as trichloroethylene (TCE) and tetracholoroethylene (also known as perchloroethylene or PCE). TCE was widely used as a solvent in industries such as aerospace and electronics, but in recent years a relatively small number of businesses, primarily in metals processing, have continued to use it. It is still found in consumer products such as gun cleaner and plastic cement. PCE is still widely used in dry-cleaning and automotive servicing.

While individual scientists and some U.S. states, such as Massachusetts and Colorado, have been addressing vapour intrusion since the since the 1990s, vapour intrusion started to become a standard part of contaminated-site response in 2001, when U.S. EPA's Resource Conservation and Recovery Act program stipulated such an assessment for all Environmental Indicator human health decisions. In early 2002, the *Denver Post* brought national attention to the problem with a landmark series on vapour intrusion. Since then many environmental regulatory agencies across the country have developed technical and policy guidance for investigating and mitigating toxic gas vapours. As researchers and regulators learn more about how vapour intrusion manifests in the real world of homes, businesses, schools, and other buildings, new strategies for vapour response are continuously rising to the surface. We expect U.S. EPA's long-awaited vapour intrusion guidance documents to be promulgated later this year.

COMMUNITY RESPONSE

American communities are diverse, so their reaction to vapour intrusion investigation varies enormously. In general, however, building occupants and owners believe the term "intrusion" is apt. Toxic, cancer-causing substances are intruding into their homes without their permission and often without their knowledge. Particularly where children are present, people are concerned about the health consequences of exposure. Owners of residential property also worry that the presence of indoor toxic substances, or even just subsurface contamination, creates a stigma and undermines property value. In fact, some property-owners don't want hear about vapour issues because they believe any hint of contamination will drive down their property values. Then there are the owners of commercial property, who fear that discovery or even the search for toxic vapours will interfere with business conducted on site.

ENGAGING THE PUBLIC

There are three key elements to working with the public at vapour intrusion sites: Building trust, supplying information, and providing opportunities for input. Siegel will provide both positive and negative case studies of each.

Building Trust

The number one factor affecting American communities' attitudes toward technical solutions at hazardous waste sites of all type is trust. If people are given information early and often, if they are heard, and if responsible parties and regulators demonstrate that they trying to protect the public, people are more receptive to official proposals, are more likely to provide constructive input, and are more likely to let consultants drill holes in their floors. Oftentimes events before and beyond the vapour intrusion response must be addressed because they influence the level of trust.

Supplying Information

Vapour intrusion investigations based upon multiple lines of evidence are like rocket science. Most people have trouble understanding why vapour intrusion occurs, how sampling and analysis is done, and how mitigation works. But the presenter's extensive experience shows that it is possible to provide the public with simple but accurate information. Such community education also includes opportunities for more devoted members of the public to learn more directly from the presentations of technical experts.

Opportunities for Input

The people who live, work, or otherwise occupy buildings with known or potential vapour intrusion have a right to offer input into environmental responses. In fact, their site-specific knowledge may provide valuable to those making cleanup decisions. Common strategies for enabling and encouraging public engagement, such as advisory groups, technical assistance, and cooperation with community-based organizations, not only help bring the public to meetings and other events, but they promote cooperation.

COMPLICATIONS OF AMBIENT SOURCES IN ASSESSING VAPOUR INTRUSION RISKS

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INTRODUCTION

The Australian Petroleum Vapour Intrusion (PVI) Guidance (CRC CARE, 2013) presents a tiered approach to assessing potential health risks due to vapour intrusion. This tiered approach allows for the assessment of indoor air data as one of the final tiers of assessment after a robust assessment of soil, groundwater and/or soil vapour data. While indoor air is the direct exposure media, the assessment of indoor air data can be complicated by the presence of secondary sources. This study presents ranges of Australian ambient levels of petroleum hydrocarbons (with focus on benzene) in indoor air.

A review of indoor air data collected from six (6) petroleum service station retail shops or adjacent buildings was conducted. Potential indoor secondary sources of petroleum hydrocarbon compounds such as benzene can originate from sources such as cigarette smoking, cigarette cupboards, building materials and furniture, stored solvents and various human activities. Indoor concentrations are also affected by ambient outdoor levels (WHO, 2010).

A tiered approach to assessing vapour intrusion risks was applied to each of the study sites. Shallow light non-aqueous phase liquid is present at each of the sites and is situated beneath an existing building. Elevated petroleum hydrocarbon concentrations relative to Tier 1 screening criteria in close proximity to an existing building were identified during sub-surface vapour sampling events. Given the uncertainty associated with applying the soil vapour data collected outside the building to workers in the building, further sampling of soil vapour and indoor air was completed to evaluate this pathway.

The objective of the indoor ambient air sampling was to assess the potential presence of petroleum hydrocarbon vapours that may be volatilising from sub-surface impacts into indoor air.

METHODS

Indoor air samples were collected from inside the existing buildings using Summa canisters or Radiello® tubes in accordance with the PVI Guidance (CRC CARE, 2013). The sampling locations were selected to target the most frequently occupied areas of buildings. Background ambient air samples were also collected from outside the buildings at a sub-set of the study sites. Samples were collected at the same locations for both day and night over the duration of a standard shift. Thus, the indoor air sampling was undertaken during business hours at "normal" operating conditions as well as during night-time conditions. The air-conditioning systems are continuously operational and entrance and exits are closed when not in use.

RESULTS AND DISCUSSION

Benzene was detected in four of the six indoor air spaces. The other key compound of potential concern (COPC) routinely detected was toluene. The indoor air results for all COPCs from all sites were below risk based levels in all indoor air samples. Comparing the indoor air results to ambient air or sample results indicative of ambient air indicate that the detections in indoor air are more likely related to other sources than the sub-surface impacts (See Table 1).

The indoor air results are also consistent with ranges of benzene measured in ambient air reported in literature. From a study of potential risk of ambient air concentrations of benzene, toluene and xylene in service stations, results indicated low risk from lifetime exposure to benzene concentrations in the offices of service stations was 1.6 – 20 ug/m^3 (Edokpolo *et al.*, 2014). Results from the study sites were towards the lower end and similar to background.

Table 1. Benzene Indoor air sample results compared to background

Study Site	Study sites range ambient/outdoor air concentration (ug/m^3)	Study sites range indoor air concentration (ug/m^3)
Site A	4.2	4.8 – 5.7
Site B	Not measured	<1.5 – 13.1
Site C	1.9	<1.6^A
Site D	Not measured	<4.8 – 9.5
Site E^B	<0.5	<0.5
Site F	Not measured	<0.8 - 1.2
Range of indoor air concentrations from Edokpolo *et al.* (2014)	0.71 - 190	1.6 – 20
Background (CRC CARE, 2013)	Roadside = 3 CBD = <3 Melbourne 1.5 – 5.5	Melbourne 4 – 7

Note: Benzene health based levels are 4.8 ug/m^3 for residential and 18 ug/m^3 for commercial.
A – Measured from a basement
B – Residential indoor air. All other indoor air results are commercial indoor air.

Cigarette cupboards and outdoor sources were the predominant influences on the indoor air concentrations. The results of the indoor air studies illustrate the complication of finding concentrations of key COPCs in indoor air from non-subsurface sources.

CONCLUSIONS

While the indoor air results indicate concentrations are below health based levels, the results also indicate that indoor air measurements are routinely affected by ambient sources and with respect to benzene at levels close to health based screening criteria.

The levels of benzene detected in indoor air in the studies are consistent with the published ranges of ambient air levels (CRC CARE, 2013 and WHO, 2010). The presence of other volatile organic compound sources complicates the assessment of potential risk relative to vapour intrusion from sub-surface sources. The results of the indoor air assessments show that a robust understanding of the site conceptual site model is essential to understanding when indoor air data may be required and how to interpret the indoor air data. Collection of indoor air data alone could result in the interpretation that a pathway existed and results in unnecessary mitigation or further assessment. The studies underscore the value of understanding the potential vapour intrusion pathway (e.g. source, sub-surface conditions and sub-surface vapour concentrations) prior to sampling indoor air.

REFERENCES

Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) (2013) Petroleum Hydrocarbon Vapour Intrusion Assessment: Australian Guidance. Technical Report No. 23. July 2013.

Edokpolo, B., Yu, Q.J. and Connell, D (2014) Health Risk Assessment of Ambient Air Concentrations of Benzene, Toluene and Xylene (BTX) in Service Station Environments. *International Journal of Environmental Research and Public Health*. 1660-4601.

World Health Organisation (2010) Guidelines for Indoor Air Quality: Selected Pollutants.

VAPOUR INTRUSION — THE VALUE OF STRINGENT NOTIFICATION AND REPORTING REQUIREMENTS IN THE MANAGEMENT OF COMMUNITY RISKS

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INTRODUCTION

Vapour intrusion (VI) is a key exposure mechanism for environmental contaminants in many countries including Australia, and is of particular significance in localities with current or historical mixed commercial and residential land use. VI processes have the potential to impact upon a large number of properties remote from the sources of contamination. Dry cleaning operations, small industrial operations and service stations in mixed-use areas can create extensive plumes of contamination, spreading beneath residential structures and presenting vapour risks to human health. Ongoing urbanisation and redevelopment of former commercial property in Australian cities have placed a media spotlight on the risks posed by vapour intrusion and have placed pressure on responsible authorities to manage these risks appropriately.

Notification to the regulatory authorities is sometimes a jurisdictional requirements aimed at assisting in managing these risks. Incorporation of mandatory notification measures requires consideration so that both public health is protected and the burden on landowners is reasonable. Specific regulatory VI guidance is not available for the State of Victoria, Australia, but environmental contamination policy makes reference to the National Environment Protection (Assessment of Site Contamination) Measure 1999 (NEPM) and follows the general approach of measuring volatile organic compounds in soil vapour, indoor/outdoor air and then using multiple-lines-of-evidence to assess potential vapour risk. However, no overarching reporting or notification requirements for VI are established. Reporting (notification) requirements are established in international jurisdictions, particularly the State of New Jersey (NJ), USA, which outlines the authorities to be informed, documentation required and timeframes for submission.

This paper explores the pros and cons of reporting requirements by comparing the statutory frameworks of the State of Victoria, Australia and the State of NJ, USA. The author notes that environmental regulatory frameworks differ considerably between NJ and Victoria and comparison of the two are beyond the scope of this document.

METHODS

The author undertook a comparison of statutory framework requirements for VI in Victoria, Australia and New Jersey, USA, identifying the presence or absence of regulatory processes in each jurisdiction and the ramifications for the management of human health risks from VI. The key documents that present VI guidance relevant to these two jurisdictions are:

- New Jersey Department of Environmental Protection (2013) Site Remediation Program, Vapour Intrusion Technical Guidance (Version 3.1) March 2013. (hereafter 'NJDEP'); and
- National Environment Protection (Assessment of Site Contamination) Measure 1999 (2013), Guideline on Site Characterisation Schedule B2. (hereafter 'NEPM').

RESULTS AND DISCUSSION

Table 1 below shows the principle differences between the Victoria and NJ jurisdictions with respect to reporting and their qualitative usefulness for the management of human health risk from VI.

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Table 1. Comparison of the Scope of Victorian and NJDEP VI Guidance

Guidance Item	NEPM/Victoria	NJDEP	Useful for Management of VI Risk
Assessment[+]			
Multiple-lines-of-evidence approach	✓	✓	✓
VI investigation triggers	✓	✓	✓
VI screening levels	✓	✓	✓
Reporting Requirements			
Submission of analytical data to regulator/Health Dept.	×	✓	×
Submission of VI Receptor Evaluation	×	✓	×
Submission of VI Sampling Results	×	✓	×
Reporting of Immediate Environmental Concern (NJDEP)/immediate threat to human health (SEPP)	×[a]	✓	✓
Property Use Restrictions	b	✓	✓
Communication to Public	c	✓	×

[+] Not a comprehensive list of VI assessment items.

[a] Immediate threat to human health and preclusion of beneficial uses are captured in the Victorian State Environment Protection Policy (SEPP) but there is no reporting requirement.

[b] Property use restrictions may be captured in planning schemes where the planning authority must satisfy itself that the environmental condition of the land is, or will be, suitable for the intended use. Where issues are identified, property use restrictions may apply.

[c] Community consultation may be required by EPA Victoria although there is no specific guidance for VI issues.

Table 1 shows that Victorian statutory framework relies on regulatory drivers that are not specifically related to VI, but rather contaminated land in general. The NEPM and Victorian state environmental policy do not provide for reporting of VI risks. However, clean-up or management is stipulated in the SEPP where there is an immediate threat to human health or preclusion of beneficial uses. Nonetheless, the driver for notification leading to implementation of clean-up or management, particularly when analytical results from a site indicate potential off-site impacts, is absent. Comparatively, the NJDEP requires consultants to notify state government and health officials from the initial VI assessment stage through to the identification of a vapour concern. Whilst these reporting requirements do not necessarily improve the management of VI risk, they do add to bureaucratic load.

CONCLUSIONS

The regulatory framework for VI in Victoria does not provide for direct reporting, but instead relies on other drivers to initiate management of risks such as capture during the planning process or identification and follow up from EPA Victoria based on the results from audit reports. These processes rely on indirect means of VI risk reporting and there is the potential for sites with VI risk to remain unknown to authorities and therefore without appropriate control measures. In contrast the NJDEP reporting requirements are considered onerous and do not necessarily improve the management of human health risks at all stages of the notification process. An optimal approach, whereby only clearly defined potential concerns are reported may provide a balance that allows regulators to efficiently manage a portfolio of VI risks in the public's best interest.

REFERENCES

New Jersey Department of Environmental Protection (2013) Site Remediation Program, Vapour Intrusion Technical Guidance (Version 3.1) March 2013.

Department of Sustainability and Environment (2005) Ministerial Direction No. 1 – Potentially Contaminated Land and General Practice Note on Potentially Contaminated Land (DSE Practice Note).

Office of Parliamentary Council Canberra (2013) National Environment Protection (Assessment of Site Contamination) Measure 1999, Guideline on Site Characterisation Schedule B2.

Victorian Government Gazette (2002), State Environmental Protection Policy (Prevention and Management of Contaminated Land), Victorian Government Printer.

CONTAMINATED LAND REMEDIATION — DETERMINING ENDPOINTS

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INTRODUCTION

The National Environment Protection (Assessment of Site Contamination) Measure, 1999, (as amended 2013) provides a framework, based on current scientific knowledge, for a consistent assessment of land contamination across Australia. While efforts to harmonise the remediation of contaminated land in Australia are being championed by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), currently such a framework does not exist.

Harmonising remediation requirements will be difficult given the vast differences in legislative frameworks between jurisdictions and the many site-specific factors that need to be considered. However, given that uncertainty in requirements can affect liability estimates, land values, funding options, and impede property transactions, it is important to provide more certainty.

Uncertainty in identifying remediation endpoints has evolved as a particular concern. Therefore, this paper discusses key elements of defining remediation endpoints including a discussion of remediation drivers and remediation objectives based on the regulatory framework in NSW. It is evident that irrespective of the complexities, there is a clear process in deriving remediation endpoints and following this process should assist stakeholders including land owners, property developers, lawyers, and contaminated land consultants to evaluate both the need for remediation and the extent of contaminated land remediation required in NSW.

REMEDIAL DRIVERS

In NSW, there are three pieces of legislation providing specific drivers for the remediation of contaminated land.

The *Contaminated Land Management Act 1997* (CLM Act), administered by the Environment Protection Authority (EPA), addresses soil and groundwater contamination that may pose a risk under the current land use and any use that the land may be put without approval or development consent under the *Environmental Planning and Assessment Act 1979* (EP&A Act).

State Environmental Planning Policy No 55 – Remediation of Land (SEPP 55), and the associated guidelines “Managing Land Contamination - Planning Guidelines” under the EP&A Act complement the CLM Act by requiring planning authorities, typically local councils, to consider land contamination in zoning and rezoning proposals and in determining development applications. Besides ensuring that land is suitable for a proposed use, SEPP 55 also clarifies when remediation works require consent of the planning authority.

The *Protection of the Environment Operations Act 1997* (POEO Act) is a key piece of environment protection legislation that makes it an offence to pollute soil and water, including groundwater; it also enables councils and the EPA to regulate certain activities, and makes the EPA the environmental regulator for activities undertaken by a public authority.

Large scale remediation projects are often captured by the Department of Planning and Environment under the EP&A Act and the remediation works may then require both planning consent and an EPA licence under the POEO Act.

There can be a number of factors other than legislative requirements that drive the need for remediation, drive remediation objectives, and hence remediation endpoints. This can include contractual arrangements between parties as well as community related factors, adverse media attention, or campaigns and associated political pressure.

REMEDIATION OBJECTIVES AND ENPOINTS

Remediation objectives are closely linked to remediation endpoints (i.e., remediation ceases once remediation objectives have been achieved) and as both are linked to the remediation drivers listed above, communication between the relevant stakeholders is key to aligning remediation endpoints with remediation objectives and drivers. It is important for clear remediation endpoints to be established before the start of the remediation works so that the extent of remediation is clear from the outset.

Contractual arrangements between parties can lead to variable remediation objectives and endpoints which may, for instance, involve returning land to a baseline status of contamination, addressing regulatory requirements, or making the land suitable for a specified use for future sale or redevelopment. Legislative requirements on the other hand, particularly remediation objectives and endpoints as a result of regulation under the CLM Act and the EP&A Act, are typically determined via an assessment of the risk posed by the contamination; that is, the objective is to either make the land suitable for the proposed use or to mitigate specific risks identified by the EPA that are, or could be, occurring under the current and approved uses of the land. These risks typically relate to vapour intrusion, direct access to contaminated soils, and/or impacts on surface waters and groundwater resources.

In determining remedial objectives and endpoints, the EPA also considers community expectations and the principles of ecologically sustainable development. Given that regulation is risk-based, remediation endpoints are often aligned with various forms of risk management that may, for instance, range from the implementation of site-specific environmental/site management plans to institutional controls to prevent the use of groundwater.

CASE STUDY

A former industrial site in Sydney has been proposed for residential redevelopment including about 300 apartments. Environmental investigations by the developer in preparation of a development application have identified significant trichloroethene contamination in soil and groundwater which has also been migrating off site. This triggered the duty to report the contamination to the EPA under the CLM Act. The presentation will use this case study to demonstrate how remediation endpoints are derived on the basis of the remediation drivers and remediation objectives specific to this site. Aspects such as the site auditor scheme administered by the EPA and the involvement of the local community will also be discussed.

CONCLUSIONS

While there is currently no national framework in relation to contaminated land remediation in Australia and there can be a wide variety of remediation drivers, objectives, and endpoints, remediation drivers and objectives can readily be identified for most sites. Once these are identified, appropriate remediation endpoints can be selected accounting for constraints such as technical and logistical constraints, and proper stakeholder engagement.

A REGULATOR'S PERSPECTIVE ON THE CLEAN UP OF GROUNDWATER AND EPA VICTORIA'S REFORM PROCESS

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INTRODUCTION

This presentation will discuss key elements of the Victorian regulatory process relating to the risk-based decision-making framework for determining whether clean up to the extent practicable has been achieved. Discussion of the evaluation and reform of the current decision making process that was completed in 2014 will be provided, as well as an appraisal of the effectiveness of the reform program associated with these regulatory decisions.

The regulation of groundwater pollution in the state of Victoria, Australia is administered through the Environment Protection Act 1970 and State Environment Protection Policies (SEPPs). The SEPP (Groundwaters of Victoria) 1997 (SEPP GoV) sets policy goals and principles relating to the protection of existing and potential beneficial uses of groundwater. Segments of the groundwater environment are defined based on background levels of Total Dissolved Solids (TDS) which identify the protected beneficial uses of each of the segments. SEPP GoV also outlines the responsibilities of the Environment Protection Authority (EPA) and details requirements for the prevention and clean up of polluted groundwater and non-aqueous phase liquid, the identification of groundwater quality restricted use zones (GQRUZs) and the ability for the Authority to determine that clean up to the extent practicable (CUTEP) has been achieved.

METHODS

To illustrate the application of the regulatory process in Victoria relating to clean up end points, a range of case studies and examples of past decisions will be discussed. Key factors in the regulatory framework that need to be considered as part of CUTEP determinations include the site location, geology, hydrogeology, proximity to sensitive receptors and the assessment of risks to human health and the environment. Appraising the type and scale of remediation at the site is a challenge in the context of the practicability of clean up. In comparing other possible remediation activities that could be used, it is important for the regulator to consider remediation practicability in terms of cost, time, logistics, technical applicability, sustainability, future generational equity and the significance of the contamination.

The probability of the realization of the beneficial uses is also a relevant consideration. The availability of a reticulated water supply, the land use at and in the vicinity of the site and potential impact to the nearest surface water receptor all need to be considered. Based on the remaining groundwater contamination, EPA also makes a determination of whether ongoing groundwater monitoring is required and can identify a zone (GQRUZ) to confirm the plume location, requiring consultation with potentially affected stakeholders.

The process of evaluation and development of the recent reform of the decision making process will also be discussed. The purpose of the project was to review and reform the determination process and assessment of CUTEP submissions provided to EPA.

During the scoping of the project, the reform team developed a set of criteria that gave environmental auditors the delegation or authority to determine CUTEP in specific circumstances for Section 53X environmental audits. As the implementation of the reform was completed in 2014, reflections on the effectiveness and outcome of the change in regulatory process over the past twelve months will be provided.

RESULTS AND DISCUSSION

Key factors in the regulatory framework that need to be considered as part of CUTEP determinations include the factual information about the site conceptual model, the nature and fate transport of pollutants compared with the relevant investigation levels and standards, allows EPA to make a decision about the technical practicability of the cleanup of groundwater. As *"the goal for any cleanup of polluted groundwater is to restore the protection of beneficial uses of the groundwater both onsite and offsite*" (Publication 840), a key part of the decision for the regulator is about the potential remaining risks to human health and the environment and, if they remain, whether these can be managed appropriately. The probability of the realisation of the beneficial uses is an important consideration in assessing the risk to human health and environment. The availability of a reticulated water supply, the land use at and in the vicinity of the site and potential impact to the nearest surface water receptor all need to be considered. During the reform process we reviewed the key decision points and developed guidance to support the decision making process.

CONCLUSIONS

The application of the regulatory framework to a wide range of sites has aided development of the current framework relating to the determination of clean up end points for contaminated groundwater. Key challenges in the decision making process included balancing the cost, time, logistics, technical applicability, sustainability, future generational equity and the significance of the contamination in the context of remediation practicability.
During the reform project we reviewed the range of changes and improvements that could be made to the CUTEP assessment process, refining the criteria for decision makers and presented the policy approach for review. We have evaluated and reformed the decision making process that was implemented in 2014. A summary of the key outcomes will be presented.

REFERENCES

EPA. 2014. *The cleanup and management of polluted groundwater.* Publication 840.1. EPA Victoria.
EPA. 2014. *Environmental auditor (contaminated land): Guidelines for issue of certificates and statements of environmental audit.* Publication 759. EPA Victoria.
EPA. 2006. *Hydrogeological assessment (groundwater quality) guidelines.* Publication 668. EPA Victoria.
EPA. 2000. *Groundwater sampling guidelines.* Publication 669. EPA Victoria.
Victorian Government. 1997. *State Environment Protection Policy (Groundwaters of Victoria)*. Victorian Government Gazette No. S 160. Government Printer, Melbourne. December 1997.

PRACTICAL IMPLICATIONS FOR REMEDIATION WASTE MANAGEMENT RESULTING FROM NEW NSW REGULATIONS AND DRAFT SITE AUDITOR GUIDELINES

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INTRODUCTION

New South Wales introduced a new Waste Regulation 2014, commencing 1 Nov 2014, which resulted in some significant changes likely to affect remediation projects. In addition, NSW Site Auditor Guidelines are under revision, and changes related to waste management will also impact on those managing remediation projects. A clear theme in both documents is the NSW EPA's objective of improving the sustainability of waste transport, treatment and disposal, clarifying the regulations and providing more controls to reduce illegal waste disposal. This paper reviews the changes and outlines the likely effects on remediation works in NSW.

PROTECTION OF THE ENVIRONMENT OPERATIONS (WASTE) REGULATION 2014

The Protection of the Environment (Waste) Regulation 2014 (the Waste Regulation) is currently in force in part, with progressive implementation through 2015 and 2016. Its main features are changes to the landfill levy, the resource recovery exemptions system, the waste tracking system, thresholds for licensing and a series of changes to improve record keeping and provision of information to the EPA. Some significant increases to penalties have also been included. Changes that may have significance for remediation works are outlined below.

Resource recovery exemptions will now apply to the user of the waste, and set conditions for use of the waste with which the user must comply. A new *Resource Recovery Order* sets conditions for the producer of the recovered waste. For remediation projects, this should increase the clarity of responsibilities and provide for better documentation from suppliers of recovered waste materials. There is also a *Draft Protocol for Managing Asbestos during Resource Recovery of Construction and Demolition Waste*, which in final form is likely to have a beneficial effect on the reliability of the quality of recycled aggregate.

The new *proximity principle* means that wastes (other than restricted solid waste) destined for landfill must go to a site within 150 km radius of the waste's generation, or to one of the two nearest if no suitable facility is available within 150 km. This may restrict options for remote remediation projects. There is a loophole where a waste generation site is nearer a state border than a landfill, in that the border provides a 'cut off'; the waste may be transported interstate and there is no limit on how far the waste is then transported. This is likely to have most effect near the NSW-Queensland border.

The *Landfill Levy* will apply to all licensed facilities from 1 Aug 2015. This is unlikely to change costs for soil disposal, as its effect is primarily on accounting requirements for operators. However, in order for the system to function, all levyable facilities must install *weighbridges* by 1 Feb 2016. This will probably be helpful for remediation managers in that it should improve records from treatment and transfer facilities which may previously not have provided good quantitation of waste receipts.

There are also new requirements for notification of the EPA about *asbestos wastes* from 1 July 2015. Information on quantity, date of movement and details of the receiving facility will have to be provided before moving the waste, and the facility then has to confirm receipt of the wastes to EPA.

NSW SITE AUDITOR GUIDELINES – DRAFT 3RD EDITION

The draft 3rd edition of the NSW Site Auditor guidelines currently include new requirements for the Auditor to check compliance with respect to off-site waste disposal and with resource recovery requirements. The Auditor will be required to notify NSW EPA immediately on becoming aware of any non-compliance with licensing or resource recovery provisions. Requirements to check are likely to include checking whether the exemption conditions have been complied with for material imported to site and for the use of material off-site where site materials are recovered for use. This will include sampling and testing requirements, and also whether the site where the material is used has done so in accordance with exemption conditions. The latter may potentially result in significant additional effort and delay compared to current circumstances.

CONCLUSIONS

NSW has introduced some significant changes to the waste regime, and is likely to continue to do so. Increasing use of Site Auditors to monitor the waste industry seems a likely development and progressive tightening of controls on the waste industry is predicted. For the remediation industry the current changes are likely to come with minor cost increases for the most part, but quite significantly increased management effort in record keeping, tracking and reporting. Some improvements are also likely since improved record keeping by waste facilities is likely to make obtaining good quality information on waste receipts and destinations easier and hopefully quicker.

ENVIRONMENTAL AUDIT REFORM: IS IT JUST ABOUT THE RED TAPE?

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INTRODUCTION

The Environmental Audit System is administered by the Environment Protection Authority (EPA) Victoria under the *Environment Protection Act 1970* (EP Act 1970). This includes appointing environmental auditors and the review of environmental audits undertaken. An environmental audit assesses the nature and extent of harm, or risk of harm, to the environment that may be posed by an industrial process or activity, waste, substance or noise.

The aim of the reform of the Environmental Audit System was to better manage contaminated sites using a more risk-based approach to regulation. In 2012, EPA and the Victorian Competition and Efficiency Commission (VCEC) undertook a joint pilot study. Its purpose was to review and identify opportunities to improve risk-based regulation in the area of environmental auditing of contaminated sites under the EP Act 1970. VCEC's review recommendations and the supporting background analysis provided EPA with direction and guidance to develop its reform program.

This presentation will discuss how the program was implemented and discuss some of the challenges and successes.

METHODS

The reform of the environmental audit systems is being implemented over three years (April 2013 to end of 2015/16) due the magnitude and number of changes proposed.

The reform program was divided into six separate project areas:

(a) Audit reform project 01 – risk appetite: establish EPA's risk appetite in relation to the audit system, supporting a consistent application of risk in decision making and roles in the audit system.

(b) Audit reform project 02 – Auditor reform: Develop and implement processes that allow EPA to adopt a more risk-based approach for the appointment and management of auditors and the associated quality assurance procedures.

(c) Audit reform project 03 – CUTEP reform: Review and implement a more risk-based approach to 'clean up to the extent practicable' (CUTEP) determinations to address concerns related to the cost, time taken and uncertainty of the process.

(d) Audit reform project 04 – Audit levels: Review and implement changes to implement a more risk-based approach to s53X audits. Support changes to policy frameworks so that 53X audit triggers are proportionate to risk and employ different levels of audits. More resources can then be allocated to higher-risk and less to lower-risk audits.

(e) Audit reform project 05 – Communications: Aims to provide clear, sufficient guidance and make information about the audit system and EPA's role available and transparent to all stakeholders.

(f) Audit reform project 06 – Procedures review: Identify those Environmental Audit Unit publications, procedures, guidelines and forms that require updating and consolidating, and put in place a program of revision to support audit reform.

The principles of the reform were to enhance the risk-based approach to the system, increase efficiencies, reduce 'red tape', and match workload to resources, while continuing to provide a high level of protection for the environment, and human health.

This was achieved by consideration of doing things differently, by changing what we do (scale), deferring tasks, or by identifying what things we could stop.

RESULTS AND DISCUSSION

A vision was developed for the program, and the vision for the environmental audit system for 2016 is "Victoria's Environmental Audit System is robust, efficient, and readily understood by its users and members of the public. It effectively protects the environment and the health of all Victorians while efficiently supporting economic development".

Do things differently

EPA's risk appetite in relation to the audit system was implemented, and this supported a consistent application of risk in decision making and in roles in the audit system. Annual auditor statements were developed to gather data on auditor activities. Our initial appointment of contaminated land environmental auditors were harmonised with New South Wales' system. S53V environmental audit reports were published to EPA's website.

Scale

The program of review of environmental audits was changed to a risk based quality assurance system. Appointments of auditors were lengthened. Some key clean up to the extent practicable (CUTEP) decisions were handed back to environmental auditors, rather than EPA. The number of procedures to implement the system was significantly reduced.

Defer

The initial appointment process was initially deferred for environmental auditors, but the contaminated land auditor's initial appointment process was recently implemented. Auditors have been appointed for longer appointment periods.

Stop

EPA has stopped maintaining environmental auditor's expert support team. Extensions of environmental auditors have been reduced significantly. Non Victorian environmental audits are no longer reviewed as part of environmental auditor's subsequent appointment.

CONCLUSIONS

Implementation of the reform program has already improved EPA's internal efficiency and reduced regulatory burdens for industry (red tape). It is estimated that the reforms implemented in 2013–14 have saved industry approximately $3.96M per year.

REFERENCES

EPA. 2014. *2013-14 Audit reform*. Publication 1578. EPA Victoria.

Environment Protection Act 1970.

Minister for Environment and Climate Change, 2013. *Reducing Red Tape Statement of Expectations for the Environment Protection Authority*. Ref MBR022188, Minister for Environment and Climate Change.

NSW *versus* WA
WHO IS BETTER AT REGULATING CONTAMINATED LAND?

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INTRODUCTION

The need for a nationally consistent framework for the regulation of contaminated land has been recognised by regulators and industry.[i] Achieving this goal will be easier said than done, particularly as there are diverse and entrenched regimes in place across each State and Territory of Australia.[ii]

This presentation will compare the statutory regimes for regulating contaminated land in New South Wales and Western Australia. In particular, the aspects of each regime which should and should not be included any nationally consistent framework will be identified.

The key topics which will be considered when comparing the two regimes are outlined below.

RESPONSIBILITY FOR REMEDIATION

Both the *Contaminated Land Management Act 1997* (NSW) (**CLM Act**) and *Contaminated Sites Act 2003 (WA)* (**CS Act**) contain hierarchies of responsibility for the remediation of contaminated land. In both jurisdictions, the polluter is primarily responsible. Failing that, liability is imposed on the owner or occupier of the land and any entity who changes the use of the land to a more sensitive use. In both jurisdictions, there is also the possibility that a mortgagee may be liable for investigation and remediation works.

However, there are different systems for determining who pays the costs of remediating and managing contaminated land. These differences relate to, amongst other things:

(a) The role of the Contaminated Sites Committee in WA (**CSC**) in determining who is responsible for remediation, as opposed to the EPA in NSW; and

(b) The ability of those found to be responsible to challenge that determination on its merits.

In WA, consideration was recently given to allowing decisions of the CSC regarding responsibility for remediation to be appealed to the State Administrative Tribunal on their merits.[iii] The public submissions were overwhelmingly in favour of this potential reform. However, as a consequence of the costs and delay which can be associated with merits review proceedings, the WA Government will not be introducing the reform.

The recent decision (which has been appealed to the Western Australian Court of Appeal) of *Coffey LPM Pty Ltd v Contaminated Sites Committee*[iv] highlights the absence of a right to seek a review of the merits of decisions made by the CSC in WA. In contrast, the decision of *Jeffman Pty Ltd and Lawrence Dry Cleaners Pty Ltd v Environment Protection Authority of NSW, Sydney Water Corporation and Ors*[v] demonstrates the benefits of merits review rights.

The lessons for regulators and consultants of both decisions will be discussed.

PLANNING APPROVAL FOR REMEDIATION WORKS

The landuse planning process remains the most effective mechanism for the identification and subsequent management of unknown or unregulated contaminated sites.

In NSW, *State Environmental Planning Policy 55 - Remediation of land* (**SEPP 55**) outlines when planning approval is required for remediation works. It also requires that remediation works meet certain standards and notification requirements and sets out the circumstances in which contamination is to be considered prior to issuing a planning approval. SEPP 55 is the key tool used by local governments to regulate remediation works and development on contaminated land, regardless of whether or not that land is being regulated under the CLM Act.

In WA there is no statutory planning policy which sets out when and remediation works are to be carried out. In circumstances where land is classified as “contaminated – remediation required”, the local government (or in the case of a subdivision approval, the Western Australian Planning Commission) is not to approve development on that land without first seeking and taking into account the advice of the chief executive officer of the Department of Environment Regulation.

However, arguably it is the sites which are contaminated, but are not regulated by the CS Act which present the greatest risk, particularly when they are proposed to be developed. It is these sites which local governments will have the greatest difficulty identifying and regulating through the planning process. Useful guidance is available to local governments[vi] assessing applications for development approval, and Part IV of the *Environmental Protection Act 1986* (WA) ensures that contamination is considered when region and town planning schemes are created and amended.

However, the absence of a legislative tool which assists local governments to identify and regulate contamination through the planning process increases the potential for the exacerbation of contamination by mum and dad (as well as other) developers.

TRANSACTIONS INVOLVING CONTAMINATED LAND

Information regarding any site which has been reported to the EPA in NSW is freely and easily available on the EPA’s website. In WA, this is only the case for sites which have been classified as ‘contaminated’. This is significant, as the DER has a backlog of reported sites which have not been classified, and therefore are not identified on a public register which can be easily accessed by potential purchasers.

Notwithstanding these differences in the availability of information and the duty to disclose it, purchasers of contaminated land in both jurisdictions may also have claims under the Commonwealth and State laws for false or misleading representations concerning the characteristics of the land or for misleading or deceptive conduct. In addition, once a site is classified as contaminated under the WA legislation, a notification is required to a purchaser 14 days before settlement of the sale. Failure to provide this notice may give rise to a claim for damages and a criminal offence.[vii]

In a transaction involving contaminated land regulated in NSW, liability under the CLM Act cannot be transferred. Although, the costs of complying with obligations imposed by the CLM Act can be contractually assigned. This is different to the position in WA, where persons responsible for remediation may transfer all or part of their liability with the agreement of the Minister.[viii] Although, it should be noted that obtaining the Minister’s consent requires the purchaser to disclose detailed financial information and take on an indeterminate liability, this aspect of the WA legislation is infrequently applied.

There may be some practical issues with the implementation of this aspect of the CS Act. However, the potential for a purchaser to take on responsibility for legislative compliance has the potential to give new meaning the concept of an 'as is where is' sale of a contaminated site and remove complex contractual indemnities and releases which invariably result in protracted negotiations.

CONCLUSION

The CLM Act and the CS Act both contain useful tools.

However, for those potentially liable to remediate contaminated land, the key advantage of the NSW regime is the right to appeal the merits of a Management Order to the Land and Environment Court. While the possibility of a right of appeal of decisions of the CSC has been discussed in WA, it did not form part of the recommended changes to the CS Act in the Minister’s recent report on the outcome of the 5 year review of the CS Act.[ix] This was an opportunity missed by WA, which should not be left out of any national framework for the regulation of contaminated land. The liability associated with remediating contaminated land is significant. There needs to be a high degree of confidence that it has been correctly determined.

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[i] Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report series, no. 22 June 2012

[ii] It is noted that there is a national consistent a framework for the assessment of contaminated sites (namely the NEPM), but no such framework for the regulation of contaminated sites

[iii] February 2015, DER, Review of the Contaminated Sites Act 2003, available at http://www.der.wa.gov.au/images/documents/your-environment/contaminated-sites/Review-of-contaminated-sites-act.pdf

[iv] [2014] WASC 504

[v] [2011] NSWLEC 89

[vi] Such as the March 2005 draft of the Contaminated Sites and the Landuse Planning Process, authored by the predecessor to the Department of Environment Regulation, available at http://portal.appealsconvenor.wa.gov.au/pls/portal/docs/PAGE/DOE_ADMIN/GUIDELINE_REPOSITORY/030305_BM_CONTAMINATED%20SITES%20AND%20THE%20LANDUSE%20PLANNING%20PROC.PDF

[vii] Section 68 of the CS Act

[viii] Section 30(1) of the CS Act

[ix] Review of the Contaminated Sites Act 2003, February 2015

BIOPHYSICAL APPROACHES TO REMEDIATION OF HEAVY METAL(LOID) CONTAMINATED SOILS

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METAL(LOID) INPUT

Soil represents the major sink for heavy metal(loid)s released into the biosphere through both geogenic (i.e., weathering or pedogenic) and anthropogenic (i.e., human activities) processes. Unlike organic contaminants, metal(loid)s such as arsenic (As), cadmium (Cd), chromium (Cr) mercury (Hg) and lead (Pb) do not undergo microbial or chemical degradation and the total concentration of these metal(loid)s in soils persists for a long time after their introduction. The dynamics of metal(loid)s in soils depend not only on their physico-chemical interactions with inorganic and organic soil constituents, but also on biological interactions largely associated with the microbial activities of soil-plant systems.

METAL(LOID) DYNAMICS AND BIOAVAILABILITY

Microorganisms control the transformation (microbial or bio-transformation) of metal(loid)s by various mechanisms that include oxidation, reduction, methylation, demethylation, complex formation, and biosorption. Microbial transformation plays a key role in the behavior and fate of toxic heavy metal(loid)s, especially As, Cr and Hg in soils and sediments. Microbial transformation processes can influence the solubility and subsequent mobility of these metal(loid)s in soils by altering their speciation and oxidation/reduction state. These processes play a major role in the bioavailability, mobility, ecotoxicology, and environmental health of these metal(loid)s. For example, recently, As contamination of surface- and ground-waters, mediated through redox reactions of geogenic As, became a major socio-political issue at several points around the globe.

APPROCHES TO REMEDIATION

For diffuse distribution of metal(loid)s (e.g. fertilizer-derived Cd input in agricultural soils including paddy soils), remediation options generally include amelioration of soils to minimise the metal(loid) bioavailability. Bioavailability can be manipulated through both chemical and biological approaches. For example, bioavailability can be minimised through immobilisation of metal(loid)s using a range of inorganic soil amendments, such as lime and phosphate compounds, and organic soil amendments, such as biochar. Reducing metal(loid) availability and maximizing plant growth through inactivation may also prove to be an effective method of *in situ* soil remediation on industrial, urban, smelting, and mining sites. The more localised metal(loid) contamination found in urban environments (e.g. Cr contamination in timber treatment plants) is remediated by metal(loid) mobilization processes that include phytoremediation and chemical washing. Removal of metal(loid)s through phytoremediation techniques and the subsequent recovery of the metal(loid)s (i.e. phytomining) or their safe disposal are attracting research and commercial interests. However, when it is not possible to remove the metal(loid)s from the contaminated sites by phytoremediation, other viable options, such as *in-situ* immobilisation should be considered as an integral part of risk management.

Since bioavailability is a key factor for remediation technologies, *in-situ* (im)mobilization through chemical and biological approaches may offer a promising option. In this presentation, after a brief introduction of sources of metal(loid) inputs and their dynamics in soils, the significance of chemical and biological approaches in the (im)mobilization of metal(loid)s in soils in relation to managing their remediation, will be discussed using case studies.

ME12

APPLICATION OF A TOXICITY APPROACH TO EVALUATE FREE CYANIDE AND METAL CYANIDE COMPLEXES IN WATERS OF GOLD AND OTHER MINING

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INTRODUCTION

Cyanide has been used for over a century worldwide for gold extraction. The extraction residues are discharged into tailing storage facilities (TSFs) and may cause bird mortality, particularly migratory birds, if there is exposure to cyanide-bearing waste water exceeding the toxic threshold from highly toxic free cyanide ($HCN + CN^-$) and that released from weak acid dissociable (WAD) metal-cyanide complexes.

The International Cyanide Management Code (ICMC 2006) has deemed 50 mg/L of WAD cyanide released into TSFs to be safe for wildlife protection based on observations of an apparent lack of toxicity rather than a toxicological approach. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS 2010) identified that there is a lack of toxicity data to properly assess the environmental significance of cyanide levels at gold mines.

The aims of this study are to evaluate the suitability of *Euglena gracilis* Z and SMZ strains to assess the toxicity of free cyanide and both strong (cobalt) and weak (zinc, copper and nickel) acid dissociable metal-cyanide complexes that may be present in TSFs. In addition, the toxicity response of free cyanide and copper and zinc cyanide complexes is assessed using a young chicken bioassay model with the University of Queensland Animal Ethics Committee approval (AEC No. SVS/365/13/ANNANDALE). Background to toxicity issues associated with cyanide use at gold mines has been reported (Noller et al. 2014).

METHODS

Bioassays using the unicellular algal species *Euglena gracilis*, were used to measure the toxicity of sodium cyanide, both strong (cobalt) and weak (zinc, copper and nickel) acid dissociable metal-cyanide complexes that may be present in TSFs. The two strains of Z and SMZ cells have plant-like and animal-like characteristics respectively. Another unique characteristic of *Euglena* is that it can tolerate a wide range of pH values including acid pH which is similar to that of the upper gastrointestinal tract of birds where dissociation of metal-cyanide complexes takes place. For the *Euglena* toxicity, two methods for the assessment of inhibitory concentration at 50% (IC_{50}) were applied namely an optical density measurement and a modified resazurin assay. The latter gave more robust and reproducible results. Further, the chicken was used as a surrogated model for the migratory birds to determine the effects of short-term exposure to sub-lethal doses of sodium cyanide, copper-cyanide complex mixed species, zinc-cyanide complex mixed species and a gold mine tailings sample that contains less than the ICMC guideline (50 mg WAD CN/L).

RESULTS AND DISCUSSION

Table 1 gives results for CN released or metal ion concentrations for IC_{50} of *Euglena gracilis* Z and SMZ strains.

Table 1. IC_{50} concentrations for *Euglena gracilis* strain Z and SMZ after 48 hour exposure to cobalt, copper, zinc and nickel species compare with NaCN.

Toxicant	IC_{50} strain Z	IC_{50} strain SMZ
NaCN	1.24 mg CN/L	1.02 mg CN/L
$ZnSO_4$	565 mg Zn/L	1490 mg Zn/L
Zinc cyanide complex mixed species	1.61 mg CN/L	2.13 mg CN/L
$CuSO_4$	20 mg Cu/L	116 mg Cu/L
Copper cyanide complex mixed species	4.17 mg CN/L	5.54 mg CN/L
$NiSO_4.7H_2O$	146 mg Ni/L	211 mg Ni/L
$K_2Ni(CN)_4$	13.1 mg CN/L	12.1 mg CN/L
$CoSO_4.7H_2O$	>292 mg Co/L	>292 mg Co/L
$K_2Co(CN)_6$	>780 mg CN/L	>780 mg CN/L

Based on the CN released or metal ion basis it has been found that their cytotoxicity to *Euglena gracilis* at 48 hour exposure time at pH 3.5 is in the order of NaCN >~ zinc cyanide complex mixed species > copper cyanide complex mixed species > $[Ni(CN)_4]^{2-}$ > $CuSO_4$ > $NiSO_4$ > $CoSO_4$ > ZnSO4 > $[Co(CN)_6]^{3-}$. This result suggests that toxicity in tailings is mainly due to CN- released from NaCN residue and that from the metal complexes.

Based on the CN released it has been found that the toxicity in chickens is in the order of: NaCN > zinc-cyanide complex mixed species > copper-cyanide complex mixed species.

Calibration of toxicity of NaCN to *E. gracilis* against chicken showed a good relationship (correlation coefficient R^2= 0.9858 and 0.9663 for Z and SMZ, respectively) between the two models, giving a predictive equation for the safe CN level in the water that migratory birds may consume if accessing TSFs at gold mines.

No clinical signs were observed on chickens treated with tailings water contains 22 mg/L WAD CN. However, from predictive equations it was concluded that the current ICMC guideline of 50 mg WAD CN/L may not be totally safe to some bird species such as Mallard duck *Anas platyrhynchos*, American kestrel (AK) and Black vulture (BV) based on comparison with existing data for these species.

CONCLUSIONS

This study confirmed that *Euglena gracilis* Z and SMZ can be used as a screening tool to monitor toxicity of copper, cobalt, nickel and zinc cyanide complexes that are present in gold mining tailings and as an adjunct tool to chemical measurement, and may replace conventional testing of bird species. In order to use this bioassay organism for cyanide and metal-cyanide complexes assessment, further laboratory and fieldwork may be required to calibrate the toxicity of other metal-cyanide complexes with the chicken model and to evaluate the toxicity of cyanide and WAD CN considering multiple-doses. The chicken model is a good alternative because the use of wild birds for toxicity testing is not ethically possible.

REFERENCES

ICMC (2006) ICMI. International Cyanide Management Code for the Gold mining Industry.

NICNAS (2010) Sodium cyanide. Priority Existing Chemical Assessment *Report No. 31. National Industrial Chemicals Notification and Assessment Scheme*. DHA Sydney/NSW.

Noller, BN, Ng, JC, Shini, S, Breuer, PL, Sichani-Temouri, H and Alsaadi, R N (2014) Development of a toxicity approach to evaluate free cyanide and metal cyanide complexes in waters associated with gold and other mining. *LIFE-OF-MINE 2014 Conference / Brisbane*, QLD, 16–18 July 2014. pp 573- 589.

LONG-TERM IMMOBILIZATION OF As AND Pb CONTAMINATED SOIL USING WASTE OYSTER SHELLS

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INTRODUCTION

In the past, chromated copper arsenate (CCA) was used as a wood preservative against insect and microbial rotting. Because of its toxicity, the use wood with an As_2O_5 content higher than 0.1% was banned on October 8, 2007 by the Korean Ministry of Environment (Koo et al. 2008). Even though its use was banned, the soils adjacent to CCA wood treatment facilities are still contaminated with Cr, Cu and As. On the other hand, Pb contamination is a serious problem in firing range soils. Pb alloy slugs enclosed within Cu alloy jackets are the main composition of typical military-grade bullets. In recent years, much attention with regards has been directed toward Pb contamination of firing range soils. In this study, the simultaneous long-term immobilization of As and Pb in a contaminated soil was conducted for a composite soil sample composed of CCA contaminated soil and army firing range soil using stabilizing additives derived from waste materials. Waste oyster shells (WOS) in their natural and calcined state were used as the main stabilizing agents to simultaneously immobilize As and Pb in the contaminated soil.

METHODS

Contaminated Soil

The total concentrations of As and Pb in the composite soil measured by aqua regia (1 ml of HNO_3 (65%, Merck) and 3 ml of HCl (37%, J.T. Baker)) were 189 mg/kg and 8,588 mg/kg. The composite soil was classified as silty clay loam by a particle size analyzer (PSA) in accordance with the United States Department of Agriculture (USDA). The soil pH was determined at 7.64 in accordance with ASTM method D 4980-89.

Stabilizing Agent

The WOS used in this study were obtained from Tong-young City in the Republic of Korea. The collected WOS were pulverized and powdered using a hammer mill and a ball mill to obtain a fine and homogeneous powder that passes the #10 sieve (2 mm). In order to perform the calcination process, the WOS was heated at 900^oC for 2 hours in an electric furnace (J-FM3, JISICO, Republic of Korea) to transform the calcite ($CaCO_3$) into quicklime (CaO). The calcined WOS was designated as COS.

Stabilization Treatments

The As and Pb contaminated composite soil sample was treated with 0 to 20% WOS and COS. A water content of 20% was applied to the treated samples to enable full hydration. All treated samples were cured for 3 months. The effectiveness of the stabilization process was evaluated using 1N HCl extraction fluid for As and 0.1N HCl extraction fluid for Pb in accordance with the Korean Standard Test methods (MOE 2002).

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RESULTS AND DISCUSSION

As and Pb leachability were reduced with increasing WOS and COS contents (Figs. 1 and 2). The best As and Pb immobilization results were achieved after 3 months of curing upon treatment with 20 wt% COS. Specifically, a reduction in As and Pb leachability higher than 98% and 99% was attained as compared to the control sample. The COS treatment outperformed the WOS treatment.

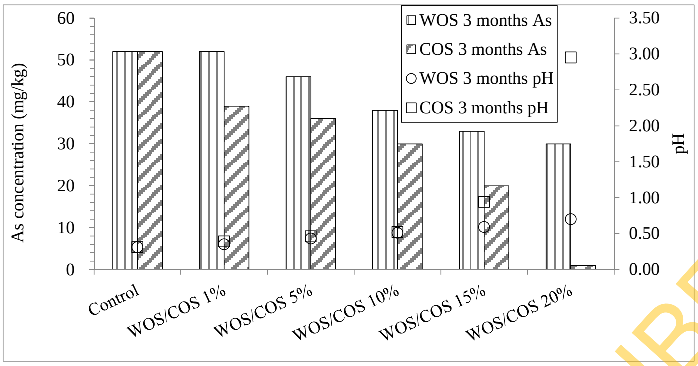

Fig. 1. As concentrations upon WOS and COS treatments

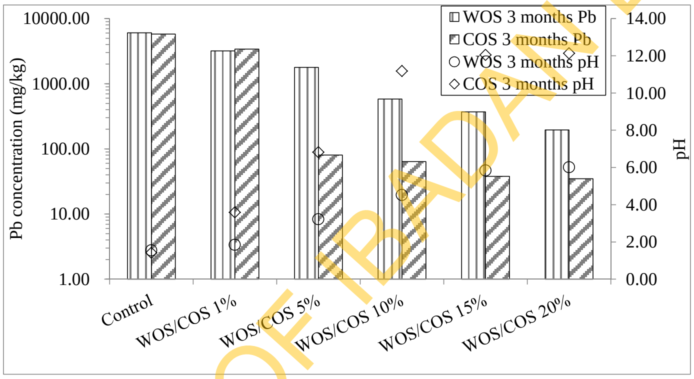

Fig. 2. Pb concentrations upon WOS and COS treatments

CONCLUSIONS

The As and Pb contaminated soil was immobilized using WOS and COS with a curing time of 3 months. A significant reduction in As (>98%) and Pb leachability (>99%) was obtained with the 20 wt% COS treatment. Moreover, the COS treatment outperformed the WOS treatment.

ACKNOWLEDGEMENT

This study was supported by the Korean Ministry of Environment as the GAIA (Geo Advanced Innovative Action) project.

REFERENCES

Koo J., Song B. and Kim H. (2008) Characteristics of the release of chromium, copper, and arsenic from CCA-treated wood exposed to the natural environment. *Anal. Sci. Technol.* 21(1):1-8.

MOE (2002) The Korean Standard Test (KST) Methods for Soils (in Korean), Korean Ministry of Environment, Gwachun, Kyunggi

A TOWNWIDE STUDY INTO THE PRESENCE AND REMEDIATION OF LEAD TAILINGS – NORTHAMPTON, WESTERN AUSTRALIA

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INTRODUCTION

Lead tailings resulting from local mineral processing were opportunistically used as a fill material during development of Northampton, primarily during the period 1950-1980. The tailings contain significant concentrations of lead (and other heavy metals such as arsenic, copper and zinc) which can cause potentially unacceptable health risks to people who may be exposed to tailings where they have been used as fill on residential, recreational and commercial properties. Following on from various previous studies and clean up works conducted by Government (on a somewhat ad hoc basis) since the early 1980's, most people living in Northampton are aware of the presence of tailings and the possible adverse health effects. However, the distribution of tailings and the number of properties affected had not previously been defined. In 2013, the State Government (Department of Lands, DoL) commissioned Aurora Environmental (Aurora) to conduct the first consolidated town-wide review and investigation to establish the extent of the issue as Phase 1 of the Northampton Lead Tailings Project (the NLTP).

Aurora worked collaboratively with the DoL (as the Government's lead agency for the NLTP), and key representatives from the Departments of Health (DoH), Environment Regulation (DER) and Mines and Petroleum (DMP). The DoL-chaired Steering Committee included representatives from these agencies and members from the Northampton Shire council representing the community. The NLTP was designed by the Government to broadly adopt the framework and approaches typically used in assessment of contaminated sites. A DER-accredited Auditor (Peter Beck from GHD) was also engaged to provide an extra level of robustness and confidence to the overall approach and project outcomes.

The main objectives of Phase 1 of the NLTP were to:

(a) determine those properties which do not have tailings present and need no further consideration in the NLTP;
(b) determine those properties which have tailings present and require remediation and/or management in subsequent phases of the NLTP; and
(c) present a summary of remediation and management options for properties where tailings were identified to support planning and budgeting for the remediation phase of the project.

The main obstacles to achieving these objectives included:

(a) community engagement and obtaining consent from land owners;
(b) achieving a scientifically robust investigation within budget limitations and using the least intrusive methods possible;
(c) elevated naturally occurring background levels of lead and other metals;
(d) implementing interim management measures on properties assessed as being at risk during the investigation.

METHODS

The scope of work for the investigation phase of the project included:

(a) detailed collation and review of all historical work undertaken on the site including obtaining further new evidence from key sources;
(b) development of sampling and analysis protocols;
(c) logistical planning including obtaining consent from property owners/occupiers;
(d) conducting inspections, interviews and soil sampling at properties within and immediately adjacent the townsite where consent had been received (701);
(e) conducting pXRF measurements from over 5,500 soil samples collected;
(f) undertaking a study into the natural background lead concentrations;

(g) undertaking a study into the bioaccessibility of lead in tailings and Northampton soils;
(h) a detailed evaluation of data quality (database creation was the key to managing data);
(i) coordinating a project steering committee and smaller technical working group;
(j) consultation with the community; and
(k) interpretation of results to classify inspected properties as either being impacted by tailings (i.e. tailings confirmed or strongly suspected present) and requiring further consideration in the NLTP or not.

RESULTS AND DISCUSSION

Of the 701 properties inspected, 95 were found to have tailings present and a further 28 were strongly suspected as having soils impacted by tailings on consideration of multiple lines of evidence. That is 123 or approximately 18% of properties investigated were found to be impacted by tailings. Tailings were found to have been placed in a variety of settings but generally conformed to logical areas associated with fill including driveways, foundations pads for structures, etc. The estimated volumes of tailings on single properties ranged from less than 1 m^3 up to approximately 1,500 m^3. The total estimated volume of tailings within the 123 properties was 11,600 m^3 (in situ).

Whilst the concentrations of other associated metals were considered during the investigation, lead was used as the primary indictor for detecting the tailings. Tailings contained lead concentrations >10,000 mg/kg, compared to natural background levels of 27-250 mg/kg in non-mineralised areas and 381-3,005 mg/kg in mineralised areas. The tailings were also visually distinctive from natural soils and other types of fill. As a result, a multiple lines of evidence approach was used to confirm the presence/absence of tailings or tailings impacts. The pXRF data was the main quantitative form of evidence, supported by qualitative lines of evidence. This approach was important in areas with elevated background levels of lead and/or mixing of tailings with natural soils/other fill. Further work in regards to bioaccessibility testing and establishing a Northampton Action Level with the DoH was also an important step into determining properties that require remedial work/ management and properties considered free of tailings impacts.

It was recognised early in the inspection and sampling program that tailings were being identified on properties in situations where there were possible unacceptable health risks posed to occupants. To avoid an unnecessary lag time between a property becoming known to have tailings and the property owner/occupant being advised of the precautions to take and remediation occurring, the DoL and DoH considered an approach of interim management measures. Aurora, the DoL and the DoH developed a matrix (later endorsed by the Steering Committee) to identify the properties where interim management measures (including a DoH staff visit, blood testing, review of practices/ behaviours at the property and notification of areas with tailings) could be employed to reduce the likelihood of people being exposed to tailings or elevated lead concentrations prior to remediation or long term management.

In the next phase of the NLTP impacted properties will be subject to either remediation through excavation and offsite disposal of tailings and impacted soils, management of tailings through in situ containment beneath existing structures and hardstand and institutional control or a combination.

CONCLUSIONS

Properties in Northampton (92% signed up to the NLTP) were able to be effectively screened for the presence/absence of lead tailings. Owners of the 123 properties found to be impacted by tailings have been notified that tailings have been confirmed or strongly suspected present. Similarly, owners of unaffected properties have also been advised of the finding for their property. Potential health risks associated with identified tailings and tailings-impacted soils are expected to be addressed through remediation and/management measures in Phase 2 of the NLTP, which is currently being considered and planned by the Government.

RECENT ADVANCES IN IN-SITU REMEDIATION TECHNOLOGIES

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INTRODUCTION

In-situ remediation techniques have been utilised by the North American and European environmental industry to remediate contaminants in subsurface environments for more than 20 years. Many early uncertainties inherent in these technologies were overcome and refined through years of development, implementation and persistence. Best-in-class implementers have tamed aggressive chemistries, developed focused injection methods and enhanced approaches by combined or sequenced delivery. Understanding the underlying chemical processes enables engineers to evaluate good conceptual site models and build focused designs that approach treatment goals with improved certainty.

Reagent delivery methods have substantially developed with many options now available. A myriad of fixed well designs and screen types are routinely used as are many proprietary pumps, direct push tooling and screens. These approaches are sometimes stymied by low conductive subsurface obstructions and lenses.

More recently the industry has focused on soil mixing delivery options for many reagents, including binding agents for contaminant stabilisation within the soil matrix. Common methods used include bucket mixing to specially designed soil mixing tools to deep soil mixing with large diameter augers attached to large rotary drill rigs. These delivery tools have unique abilities, but they all are able to eliminate the reagent delivery problems inherent with injection technologies. Limitations such as soil stability after mixing and potential overland sheeting flow of what was groundwater prior to mixing are lessons learned that assist when considering these aggressive reagent delivery options.

In-situ thermal remediation was developed by the oil industry to help recover previously uneconomic oil reserves. Electrical thermal techniques were further developed and utilised for remediation of mostly organic contaminants. These techniques, coupled with appropriate vapour treatment systems, have become widely accepted as the best-available-technology by the environmental community over the last 5 years or so. Thermal remediation has often been considered too costly for many projects requiring timelines and site accessibility-type drivers for client consideration. More recent fuel-based thermal delivery options have started to change the high cost paradigm. Additionally, vendors are developing additional capabilities and new smaller vendor companies are forcing the industry to be more competitive.

CONCLUSION

This presentation will provide an overview of each of these in-situ remediation technologies including recent advances and lessons learned from direct implementation.

IS THERE A FUTURE FOR ONSITE CONTAINMENT?

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INTRODUCTION

On-site or in-situ containment of contaminated soil is not new. The US EPA provided 560 pages of written guidance some thirty years ago in September 1985 (EPA/540/2-85/002). It was one in a series of technical handbooks issued to implement the Superfund law (CERCLA).

Australian academics contemplated containment as part of their book chapter in 1996 (PSC Rao et al.).

The Australian and New Zealand Environment and Conservation Council published its guideline in September 1999 titled 'Guidelines for the assessment of on-site containment of contaminated soil'. The guideline was intended for onsite placement only. It described the need to protect public health, environment and minimise waste to landfill.

In 2007, the South Australian Parliament amended the *Environment Protection Act 1993* (the Act) to include a definition of for remediate. The Act defines (in section 3) remediate as 'treat, contain, remove or manage chemical substances on or below the surface of the site…'. It is evident from this definition, that Parliament considered on-site containment as being a suitable remediation technique. This concept is consistent with the Objects of the Act (section 10), which are centred on the principles of ecologically sustainable development.

ASTM has provided recent (2015) guidance in relation to onsite containment. It is intended for use at sites that are presently developed or proposed for development for residential, commercial, or industrial purposes but which contain chemical-affected soil, groundwater, air, or other environmental media, which may pose an unacceptable risk to human health.

In 2010, two legal academics undertook an international review of regulatory approaches and issues with on-site containment (CRC CARE 2010). The review concluded that 'dig and dump' faces serious challenge as policies seek to reduce the flow of waste'. It described four main impediments to the adoption of in-situ containment in Australia: adequate regulatory framework, the need for institutional controls, residual liability and the overlap between con site and waste legislation.

Interestingly Fowler and Cole stated for the first time that 'it may be argued that in-situ retention is simply deferring the resolution of site contamination problems to future generations, which is contrary to the principles of ESD'.

In 2013 CRC CARE issued a technical report that considered a risk based approach to on-site containment. The report discusses the risks associated with accepting and managing residual contamination at a site, and the controls that may make the risk acceptable. The main author, Dr P Nadebaum states that 'allowing contamination to remain in-situ on sites is allowed under Australian regulatory guidance, and is already commonly practised. However, the basis for making decisions on whether it is acceptable to allow contamination to remain is not defined, and is generally made on the basis of expert judgement.'

CRC CARE is continuing to work in this area with the intention of providing a Technical Report for the Application Guide for Containment as part of the National Remediation Framework.

SOUTH AUSTRALIAN APPROACH

On-site or in-situ containment is permitted by legislation. However the hurdles identified by Fowler and Cole must be overcome. This is typically achieved through the site contamination audit process. It provides all stakeholders with a high level of confidence in the quality of the work and decision making. The site contamination audit report must accurately describe the site and the location of the containment cell(s). All site contamination audit reports must be placed on the EPA Public Register (section 109 of the Act) and be made publically available. The contents of the register are maintained in perpetuity and cannot be removed (unless authorised by Regulation from the Governor).

There are many examples of successful onsite containment in South Australia.

RELUCTANCE FOR ADOPTION OF INSTU CONTAINMENT

There are several reasons for the ongoing reluctance to the adoption of on-site containment as a remediation strategy. These include its cost, reputational risk, political risk, future liability, financial risk, project timing risk, regulatory uncertainty, potential changes of future standards, engineering risk, title blight and community dissatisfaction.

If the key stakeholders at a site are considered to be the site owner, the consultant, the auditor, the developer, the regulator and the community – all of these stakeholders need to work as a team to resolve these risks.

CONCLUSIONS

For on-site containment projects to be successful, three key stakeholders must adopt strong leadership positions.

The regulators must establish or adopt transparent and predictable technical standards for the assessment of proposals. It is anticipated that the National Remediation Framework will provide this. The regulators must also establish and maintain records that will survive for decades and perhaps centuries to come. The site contamination profession must embrace the need for technical competence every time (it is anticipated this will be achieved through certification) and work with auditors to achieve quality outcomes. The site owners must expect and fund quality outcomes, have an appetite for risk and commit to robust and transparent community engagement programs.

DISCLAIMER

The views and opinions expressed in this paper are those of the author and may not necessarily represent the views and opinions of the South Australian Environment Protection Authority.

REFERENCES

US EPA (1985) Covers for Uncontrolled Hazardous Waste Sites (EPA/540/2-85/002)

PSC Rao, GB Davis and C Johnston (1996) '*Contaminants and the soil environment in the Australasia-Pacific Region*', Kluwer Academic Publishers, Eds R Naidu et al. pp 361-410

ANZECC (1999) 'Guidelines for the assessment of on-site containment of contaminated soil'

ASTM (2015) E2435-05: Standard Guide for Application of Engineering Controls to Facilitate Use or Redevelopment of Chemical-Affected Properties

CRC CARE (2010): Technical Report 16 (Part 1): Safe on-site retention of contaminants – Regulatory approaches and issues – a legal perspective (R Fowler and D Cole)

CRC CARE (2013): On-site Retention of Contaminants Part 2: A risk-based approach, Report No. 16, (P Nadebaum)

PERMEABLE REACTIVE BARRIER:
AN EFFECTIVE IN-SITU REMEDIATION TECHNOLOGY

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INTRODUCTION

Permeable Reactive Barriers (PRBs) are an important component of established technologies for the remediation of contaminated groundwater. Since the first field-scale PRB was built in Sunnyvale, California in 1994 – 95, more than two hundred PRB systems have been installed worldwide.

A PRB treats pollutants downstream from the source zone of the contamination (“hot spot”), which may be spread over a wide area or not accurately located (Figure 1). However, it is important to know the total contaminant mass in the source area and its approximate geometry in order to assess the operational features and lifetime of a PRB relatively accurately.

A PRB divides a polluted area into two sections, i.e., cuts off a contaminated ground water plume from areas downgradient the barrier which have to be protected,: a contaminated upstream segment and a remediated or non-contaminated downstream segment (Figure 1). The upper section contains the source of the contamination and the discharging contaminated ground water plume; hence, a continuously contaminated area upstream of the barrier is tolerated. The section downstream the barrier is affected by the clean-up effect of the barrier, and hence shows decreasing and eventually vanishing contaminant concentrations over time. PRBs are therefore chiefly regarded as protective measures for safeguarding communities and environments that would otherwise be exposed to the contaminant source, or in other words, jeopardized by contaminated ground water discharging from the source in a certain distance downstream. In cases where the source becomes entirely depleted over the operational term of the PRB, the barrier may achieve an actual decontamination over time. Thus, PRBs can be regarded as both a safeguarding technique and as an actual decontamination technique, depending on the contamination scenario and its outcome during the barrier’s operational life.

Therefore, PRBs are not designed for swift remedial action of the source zone. They are designed for managing a source zone by eliminating the plume over a long period of time, accepting that the original source of the contamination and upper part of its discharging plume are not tackled. The operational lifetime of a PRB may thus range from years to decades.

Engineered PRBs

The UK and German PRB guidance documents stress that a PRB should be engineered. The US PRB guidance provides a more extended definition, which includes injection zones. Although the PRB concept was first developed in North America in the early 1990s, European projects have also played an important part in the development of the technology. The first full-scale zero valent iron (ZVI) PRBs had already been erected in Sunnyvale, California, and in Belfast, UK, in 1995. The first German full-scale ZVI PRB at Tübingen was erected in 1998, whereas the full-scale Austrian PRB at Brunn am Gebirge (a suburb of the Austrian capitol Vienna) employed granular activated carbon (GAC) in 1999. The total number of active European projects had reached around 50 by 2015, of which more than 25 were full-scale. Some European suppliers offer sophisticated turn-key solutions for PRBs, while numerous R&D trials have been performed since 2000, ranging in scale from pilot to full-scale applications.

During the evolution of the technology, two general construction types emerged:

1. The Continuous Reactive Barrier (CRB) consists entirely of a permeable zone of reactive material that is installed in the path of a contaminant plume, for instance in a trench, and captures the entire plume. Manipulation of the ground water flow or control over it or over the reactive material(s) is not possible using this construction type (1).
2. The Funnel-and-Gate system (F&G) is characterized by impermeable walls that intercept the contaminated plume and direct it towards a permeable section loaded with the reactive material (gate).

In the early nineties, it was believed that both design types would work effectively for several decades in the subsurface, even without maintenance, once installed. For this reason it was thought that PRBs did not require easy access to the reactive material or the ground water, as malfunctions were thought unlikely.

During subsequent development of the PRB technology, the F&G design has been significantly modified at numerous sites, especially across Europe, to address special issues, such as handling a heterogeneous ground water flow or intercepting several plumes originating from different sources – in other words, to exert maximum control over the flow and parts of the PRB structure. Furthermore, entirely new design features have been developed, such as Drain-and-Gate (D&G) or Trench-and-Gate (T&G) systems, where the ground water is directed towards a reactor chamber or in-situ vessels (ISVs) equipped with inserted reactors and filter pipes, or the use of gravel drainages instead of cut-off walls (1).

In Europe, D&G or “Efficiently Controllable” PRBs (EC-PRBs), where the ground water flow is directed and controlled by drainage, pipes or even by active pumping are now common. This has led to a differentiation in the European design of PRBs from their North American counterparts, where CRBs and reactive injection zones are widely used.

European PRBs are pretty often equipped with ISVs or in ground reactors or removable cartridges, which are highly accessible via shafts, and which are directly connected to drains, pipes etc. directing the contaminated ground water to the vessels and the reactive materials. In addition, modified F&G technologies (“non-classical F&G”) have been implemented, where some access to the reaction chambers is possible, that is, in the event of minor malfunctions; these may also facilitate inspection of the reactive zone to a certain degree. Also modified F&Gs, where the hydraulics can be controlled by a discharge / outlet pipe or similar measure, were erected in Europe. These PRBs can be configured to suit site-specific features and monitoring and maintenance can be controlled more effectively. Some technology providers propose a maintenance strategy based on annual operations that can range from a simple clearing of clogged sections to a full replacement of the reactive medium (particularly recommended for barriers which use the adsorption principle). For example, the French company Soletanche-Bachy uses a patented pre-fabricated three-chamber system that is inserted into a shaft or vault / cell. Its two lateral chambers are filled with gravel to passively guide / manipulate the natural ground water flow and also permit access to the reactive material, which is usually placed in the middle chamber. A PRB in Amersfoort, The Netherlands, is an EC-PRB, which passively collects the ground water through a cut-off wall, and discharges it by means of a pipe (which penetrates the cut-off wall) to a ZVI reactor located downstream.

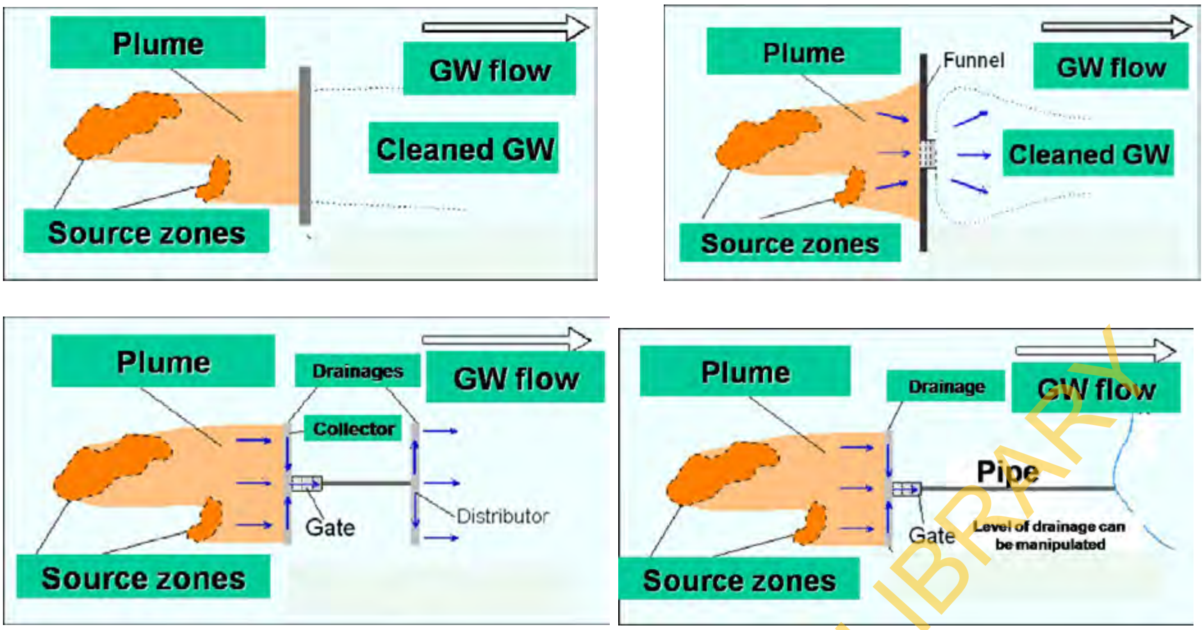

Figure 1: Comparison of the classical CRB (top, left) and F&G designs (top, right) with the D&G (bottom, left) and EC-PRB designs (bottom, right). A D&G as well as an EC-PRB may utilize drains instead of or in addition to cut-off walls to direct the ground water flow towards vessels containing the reactive materials (or a pea gravel zone where microbiological degradation takes place). In an EC-PRB, the flow can be altered by actively changing the hydraulic head or even by pumping. The two latter types may best suit sites with low ground water flows, low aquifer permeabilities and / or complex subsurface conditions, contamination scenarios etc.

This contribution provides an overview of the PRB technology as a valuable and versatile in situ remediation technology.

REFERENCES

Naidu, R. and Birke, V. (2014). Permeable Reactive Barrier: Sustainable Groundwater Remediation, CRC Press, Boca Raton, U.S.A., 333 p. ISBN 9781482224474

ME24

COMBINING IN SITU CHEMICAL AND BIOLOGICAL OXIDATION FOR GROUNDWATER TREATMENT UNDER A PERFORMANCE BASED PROJECT DELIVERY PROGRAM

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INTRODUCTION

There is increasing awareness that the challenges presented by contaminant releases to soil and groundwater are not being met by the current paradigm of single technology solutions. The objective of this presentation is to illustrate key concepts and considerations for combining in-situ chemical treatment with biological treatment to enhance accelerated project delivery at a combined Navy Facilities Engineering Command (NAVFAC)/Superfund site. Combining chemical and biological treatment technologies, both spatially and temporally, is becoming increasingly common to achieve remedial objectives that require reduction in dissolved phase concentrations by several orders of magnitude. Technical challenges include selecting the appropriate chemical and biological amendments, their concentrations and determining the sequential approach.

METHODS

The remedial goal for this site was to reduce groundwater concentrations of benzene and ethylbenzene to below commercial Remedial Goals (RGs). The dominant remedial design approach for remediation at this site focused on consistently replenishing and maintaining oxygen concentrations within the area of benzene and ethyl benzene impacts. Pre-design activities were conducted to better define the extent of the remediation zone and the applied combined remedial approach. This included a treatability study, site investigation by Membrane Interface Probe (MIP), and pilot injection test. The treatability study was conducted to determine the potential for biological remediation at the site and what amendment would be most beneficial to enhance biological degradation. An injection test was implemented using direct push technology (DPT) to determine the site-specific injection flow rates, pressures and potential radius of influence. The data was then analyzed and the full scale remedial design, using biological and chemical amendments, was developed for the site. This involved three rounds of DPT injections at 25 locations in the saturated zone over the period of one year.

CONCLUSIONS

Within nine months of implementing the combined chemical/biological oxidation remedy the concentrations of benzene and ethylbenzene were reduced by more than 90 percent from baseline concentrations. In addition to this, three of four performance monitoring wells are below the residential RGs. The site is now positioned to move towards monitored natural attenuation (MNA), ahead of the already stringent remedial goal of one year.

IN SITU REMEDIATION OF PETROLEUM HYDROCARBONS

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INTRODUCTION

Enviropacific own and operate a variety of mobile and semi-permanent remedial technologies, designed for in situ remediation of hydrocarbon based contaminants. They are utilised at a multitude of sites across Australia, encompassing varied geological environments with different contamination types, concentrations and volatilities. Application of the right remedial technology will ensure the best remedial outcome, which requires a detailed understanding of the site geology, contaminant type and concentration.

Geology: Influences the hydraulic conductivity, or the ability for fluid to flow through soil pore spaces or rock fractures, and the transmissivity, the measure of how much water can be transmitted horizontally. This information is crucial for understanding and applying the correct in situ remedial technique.

Hydrocarbon Type: Influences volatility and therefore the stripping effect caused from creating airflow through unsaturated soil pores or rock fractures. This process is the remedial driver of Soil Vapour Extraction (SVE) and the main remedial driver of Multi Phase Extraction (MPE), whereby hydrocarbon mass is removed by creating a vacuum and airflow within the subsurface environment.

Hydrocarbon Concentration: The total mass of contaminant within the site subsurface. At high concentrations it is found as free phase product or light non aqueous phase liquid (LNAPL) within the soil and floating on top of the groundwater at varying thicknesses, whereas at lower concentrations it is dissolved within the groundwater. Hydrocarbon concentration influences the remedial technology and application, and also waste stream disposal. Thermal destruction of hydrocarbon impacted off-gas is utilised for high concentrations whereas carbon treatment is commonly utilised for less impacted sites.

METHOD

After gaining an understanding of the site characteristics, a review of the most appropriate in-situ remediation approach is undertaken with consideration of:

- Cost;
- Current land use; and
- Remediation drivers.

The options for semi-permanent systems or mobile systems are then assessed on the above criteria.

Mobile Systems: Are often utilised due to being quickly deployable, low capital nature and short duration. This encompasses truck and trailer or skid mounted techniques such as MPE/SVE and in situ chemical oxidation (ISCO). MPE involves the application of a vacuum to the subsurface environment to extract liquid and vapour. This is typically done through existing 50 mm diameter monitoring wells, or purpose installed extraction wells (usually larger diameter). Vacuum is generally created via a Liquid Ring Pump (LRP) or an Internal Combustion Engine (ICE) system.

ISCO involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming contaminants into less harmful chemical species and enhancing mass transfer.

It can be used in conjunction with other in situ techniques to reduce anticipated clean up times required for natural attenuation and other remedial options.

Permanent Systems: Mobile remediation technologies can be effectively set up as automated systems for permanent applications. Cost and remediation drivers are the major considerations as to whether a system will be set up permanently or mobile events are performed.

CONCLUSION

Application of the most appropriate in situ remedial technology requires a good understanding of the site's subsurface environment with consideration of cost, current land use and the remediation driver, to ensure the best remedial outcome for the site.

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ME32

IN SITU ENHANCED ANAEROBIC BIODEGRADATION OF BENZENE BY INJECTION OF A SULPHATE BASED SOLUTION

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INTRODUCTION

An *in situ* enhanced anaerobic bioremediation technology was selected as the most appropriate remedial approach for a site in Sydney contaminated by petroleum hydrocarbons, based on the groundwater quality around the target area and existing site constraints, such as the presence of significant underground utilities.

Within the vicinity of one of the monitoring wells located downgradient of the site, there was evidence in groundwater of natural attenuation of the contaminants of potential concern (COPCs) as represented by an increase of methane and ferrous iron concentrations and a decrease of sulphate along the downgradient direction.

It was anticipated that the addition of sulphate would robustly stimulate the effectiveness of the natural attenuation conditions in the area.

METHODS

The reagent selected to stimulate the anaerobic degradation through the introduction of sulphate ions, working as electron donors, was magnesium sulphate heptahydrate ($MgSO4.7H2O$), commonly known as Epsom salt. Although biostimulation through introduction of sulphate is recognised as a longer term process in reducing benzene concentrations, the reagent has been selected in this scenario due to its high solubility, low-corrosive nature, and negligible detrimental impact on the surrounding environment (e.g. sulphate does not induce acidic conditions in groundwater as do dissolved iron solutions).

Design

The target concentration of sulphate in groundwater was calculated (based on stoichiometry, pore space volume and contaminant average concentrations) to be 2,000 mg/L, which was expected to be achieved by injecting an estimated volume of 29,300 L of a 40 g/L magnesium sulphate solution into the subsurface..

Health and Safety

A site-specific health and safety plan was prepared for the injection works, with a Hazard Operations (HazOp) review conducted on 5 November 2014. The assessment included a clean water pressure test of the system prior to the injection start-up. The main hazards identified during the review were:

(a) Traffic;
(b) Noise;
(c) Pedestrians;
(d) Manual Handling; and
(e) Pressurized hoses, pipes and fittings.

Injection Equipment

A progressive cavity pump (PCP) equipped with a variable speed drive (VSD) was selected for this job based on its ability to provide steady and adjustable injection flow rates.

Quick-connect fittings were used for the injection well heads in order to facilitate mobilisation and demobilisation tasks.

A datalogger (InSitu TROLL 9500®) was deployed 4.7 metres downgradient from the injection well before the start-up (8 December 2014) where it recorded pressure (indirect measurement of groundwater level) and groundwater quality parameters (electroconductivity, oxi-reduction potential, pH, temperature and dissolved oxygen) until 30 January 2015, when it was retrieved.

RESULTS AND DISCUSSION

The injection was conducted between 8 and 17 December 2014. Graphs generated by the data obtained during and after this period show that:

(a) Electroconductivity increased after each injection day, reacting to the presence of new ions in the local groundwater;

(b) Electroconductivity data follows the groundwater elevation, increasing as elevation increases with injection (see Figure 1 below) and decreasing as elevation increases during rainfall events (dilution);

(c) ORP readings have decreased from approximately 0 to -380 mV, showing that the injection event has contributed to create a more chemically-reducing environment and, thus, stimulating anaerobic processes; and

(d) High concentrations of sulphate were detected in MW24, MW23 (injection wells), MW208 and MW210 (downgradient from MW24), showing that the 2,000 mg/L target concentration proposed for the porous volume around the injection location during design stage was reached and even surpassed.

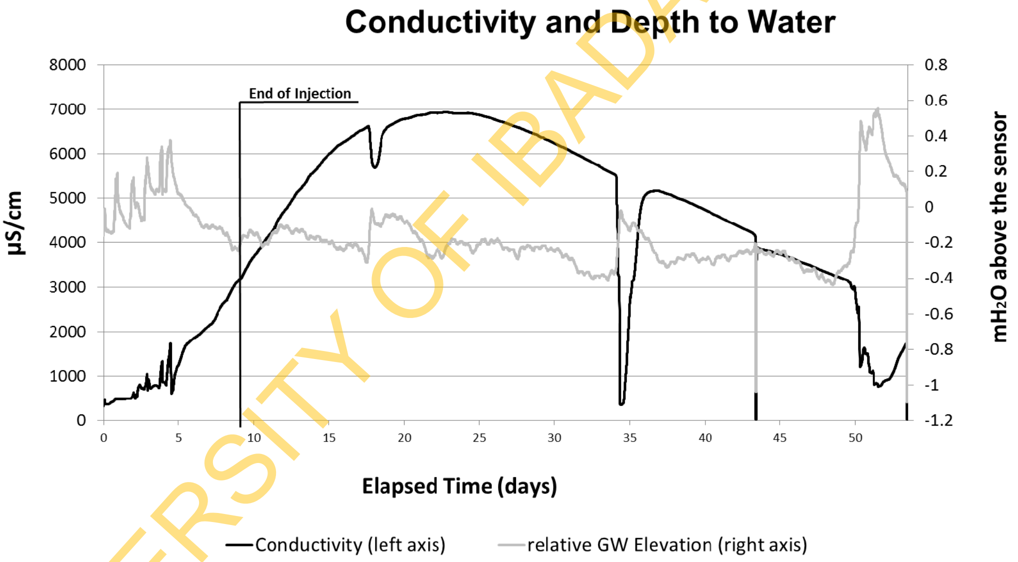

Fig. 1. Electroconductivity and Depth to Water for the whole logging period (readings taken 4.7 metres downgradient from the first injection point).

CONCLUSIONS

The results presented in this document show that:

(a) Delivery of reagents into the subsurface was uniform around the injection locations, based on depth to water and groundwater quality readings obtained from the surrounding wells during the injection event;

(b) The groundwater sulphate concentration target of 2,000 mg/L was achieved in wells MW24, MW23 (injection wells), MW208 and MW210 (downgradient from MW24), as proposed during design stage;

(c) The injection system managed to achieve and even surpass the mass of reagent injected, proposed during design stage; and

(d) The works were completed timely and safely, with no incidents or accidents recorded.

ENHANCING ISCO — STRATEGIES AND TOOLS

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INTRODUCTION

This abstract outlines the information that will be presented about the successful implementation of In-Situ Chemical Oxidation (ISCO) and focusses on the pre-remediation activities that can be performed to improve the efficiency, cost-effectiveness and feasibility of implementing ISCO. ISCO is a dissolved-phase groundwater remediation technology. Activities that define or remediate sources of dissolved-phase groundwater contamination improve the implementation of ISCO.

METHODS

There are several pre-remediation activities that can be performed to improve ISCO and are as follows:

(a) High-resolution soil characterisation;
(b) Treatment Trials;
(c) Contaminated soil remediation; and
(d) Non-aqueous phase liquid (NAPL) and residual contamination reduction.

The presentation will describe each activity and provide a case study that relates the benefits of pre-remediation activities.

High-Resolution Soil Characterisation

High-resolution soil characterisation uses the collection of numerous soil samples in a relatively dense layout; the use of laser-induced fluorescence (LIF) or a membrane interface probe (MIP) to obtain a relatively accurate understanding of the quantity and distribution of contaminant mass. High-resolution soil characterisation can be performed after ISCO to assess for remaining hotspots.

Treatment Trials

The implementation of ISCO is improved by performing treatment trials on soil and groundwater obtained from the site. The trials can be used to assess oxidant demand, optimum dosing and buffering capacity.

Contaminated Soil Remediation

In cases with relatively deep groundwater it can be beneficial to remediate soil prior to performing ISCO. The remediation of soil prior to ISCO reduces the amount of contamination that can desorb from soil into groundwater thereby reducing the mass to oxidise. The method of soil remediation can vary but the choice of technology should consider how it will affect the implementation of ISCO.

NAPL and Residual Contamination Reduction

The removal/reduction of NAPL and residual contamination improves the performance of ISCO. ISCO works on the basis of moving electrons and NAPL acts as an electrical insulator. As a result ISCO does not oxidise NAPL. ISCO can generate heat and reduce surface tension in water which can mobilise NAPL and residual contamination. If NAPL is not addressed properly then the mobilisation of contaminants can adversely affect the performance of ISCO.

NAPL removal/reduction can be performed by using technologies such as multi-phase extraction (MPE), solvent extraction, surfactant flushing and active/passive NAPL recovery.

The most effective approach is site-specific but should consider NAPL transmissivity in the case of light-NAPL (LNAPL). The utility of using mobile MPE events versus the installation/operation of a fixed MPE system should also be considered. All things being equal, mobile MPE has not proved to be as effective as fixed MPE systems.

Once the primary sources of contamination (continued leak or NAPL) are addressed, residual contamination is the source of dissolved-phase groundwater contamination. The need to re-inject is often caused by not gaining a full understanding of residual contamination or without attempting to remove or reduce it. ISCO is not cost effective if residual contamination is not properly addressed.

CASE STUDY

The results of using solvent-enhanced ISCO (SE-ISCO) along with other pre-remediation activities will be presented to demonstrate their benefits.

REFERENCES

Carvel, Douglas (2014) Critical Importance of a Conceptual Site Model in the Effective Design and Treatment of Complex Sites USA, Keynote of ISCO Innovations, Ecoforum 2014.

IN SITU CHEMICAL REDUCTION TREATMENT OF LEAD AND SILVER IN GROUNDWATER UPGRADIENT OF A DRINKING WATER SOURCE

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INTRODUCTION

Metals in groundwater can be difficult to treat and can cause toxic effects if the water is ingested. Treatment of metals in groundwater involves either extraction of the groundwater, or removal of the metals from the groundwater by causing the metals to precipitation fixation to aquifer solids.

Groundwater at a site in Brazil contained lead and silver at concentrations above regulatory criteria. The site was located upgradient of a drinking water source. In situ treatment was the preferred option since it would be more cost effective and have a lower impact on the Site. An assessment of potential remedial technologies demonstrated that in situ chemical reduction (ISCR) would be an appropriate treatment technology for the Site

METHODS

A treatability study was performed to determine the reagents for ISCR. Samples were obtained from the Site and reducing agents were screened for their effectiveness in reducing metals concentrations in the groundwater samples. Different reducing agents were added to groundwater microcosms at different concentrations and allowed to react. The groundwater was then analyzed for dissolved metals.

Based on the results of the treatability study a full scale application was performed. For the full scale application, ISCR was performed in the source area of the Site using 30 injection wells. Source zone monitoring was one week, one month, four months, and one year after injection.

RESULTS AND DISCUSSION

The results of the study showed that ISCR treatment using sodium sulfide was effective for the removal of lead and silver to below criteria.

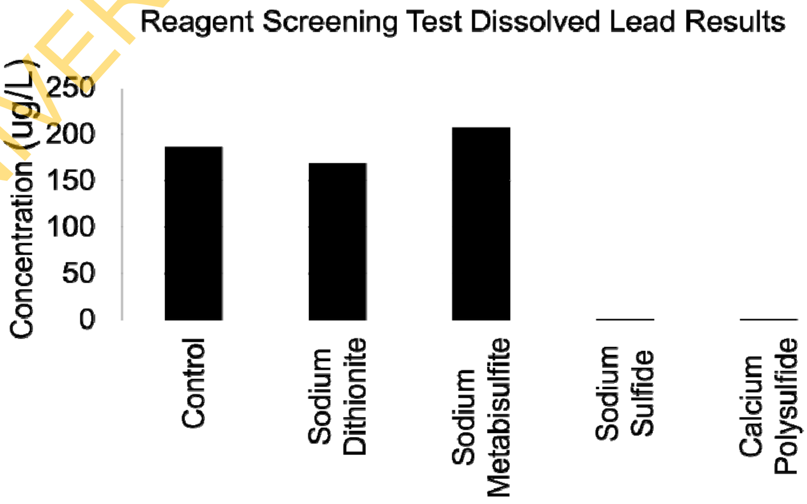

Figure 1. Reagent Screening Test Dissolved Lead Results

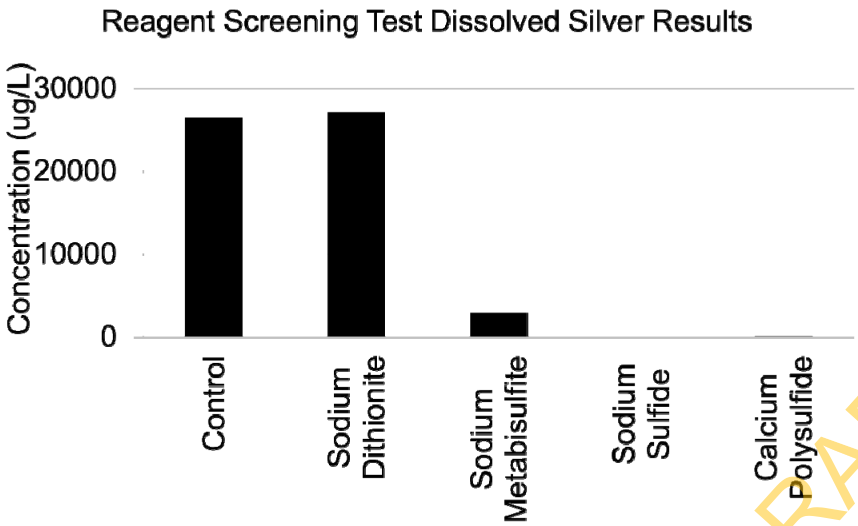

Figure 2. Reagent Screening Test Dissolved Silver Results

Based on these data sodium sulphide was selected for the full scale application. Sodium sulfide had the additional benefit of being readily available in Brazil. A sodium sulfide solution was injected into each of 30 wells in the Site source area.

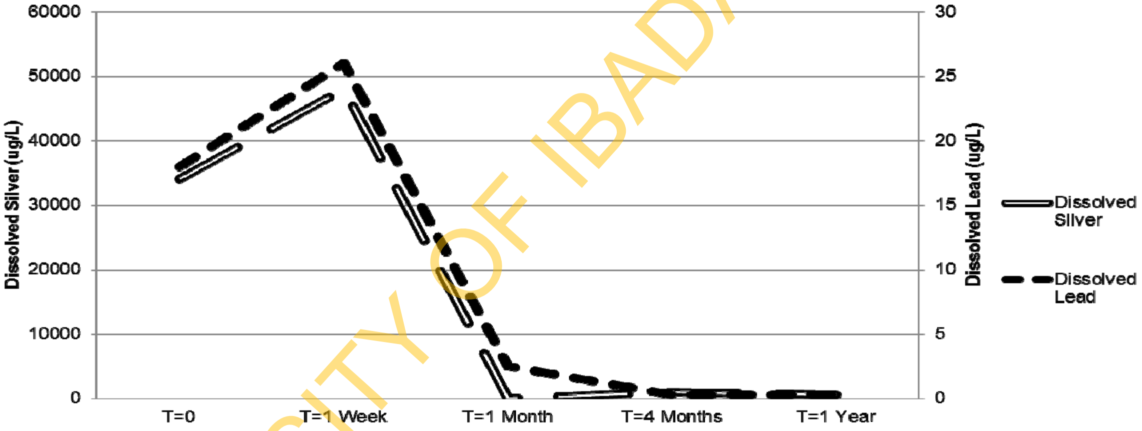

Fig. 3. Lead and Silver Concentrations after Full Scale Application

CONCLUSIONS

The monitoring showed that dissolved silver and lead had been treated to non-detect levels by the first injection of sodium sulfide. These data showed that the dissolved lead and silver have been removed from the groundwater by the treatment and further treatment is not required. Total lead and silver were detected in the groundwater due to the presence of suspended particulates in the groundwater, however these concentrations decreased as the particles settled.

MANGANESE ACTIVATED PERSULFATE (MNAP) FOR THE TREATMENT OF A SOURCE ZONE: AN INNOVATIVE DUAL OXIDANT FORMULATION

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INTRODUCTION

Geosyntec has developed a novel in situ chemical oxidation (ISCO) method utilizing manganese oxides to activate sodium persulfate (MnAP). This innovative method was developed based on the hypothesis that manganese oxides can activate persulfate as demonstrated in recent academic literature (Mushtaque *et al* (2010) and Sedlak *et al* (2014)). However, the main objective of this academic literature was to determine the impact of naturally occurring organic and inorganic components, including iron and manganese oxides, on the activation of persulfate. The mode of action of MnAP is to increase manganese oxide content within the target treatment zone via delivery of freshly precipitated manganese oxides from permanganate consumption that then act as activators for persulfate that propagate the persulfate radical-based oxidative chemistry.

Persulfate activation is typically achieved through several methods such as heat, alkaline, chelated iron and hydrogen peroxide. The activation process is usually done to propagate the sulfate radical ($SO_4^{\cdot -}$ oxidation-reduction potential E^o 2.6 V) which has a higher E^o than the persulfate anion ($S_2O_8^{2-}$ oxidation-reduction potential E^o 2.01 V). These activation methods are well understood and commonly applied when using persulfate for the oxidation of contaminants.

However, compared to the activation methods of persulfate mentioned above, persulfate activation by reactions at mineral surfaces is not as well understood. Recent studies have shown that aquifer materials such as iron and manganese oxides can potentially activate persulfate. The recent lab-based academic studies looked into the impact of different aquifer materials on the activation of persulfate, for example, Mushtaque *et al* (2010) determined that the greatest potential for persulfate activation was through an increased concentration of the mineral manganese dioxide (MnO_2). More recently, Sedlak *et al* (2014) determined that persulfate activation by naturally occurring minerals such as manganese dioxide can activate persulfate and the rate of activation would increase in zones 'rich' in iron- or manganese-oxides.

METHODS

Geosyntec has recently completed two laboratory treatability studies of MnAP that treated between 300 and 500 mg/L of trichloroethene (TCE) over 99.9% in both the aqueous and solid phases. The treatability data also showed that MnAP can achieve this level of TCE treatment using less of each of the two oxidants as compared to single oxidant approaches using typical permanganate and persulfate formulations. In addition, post-treatment pH was circum-neutral and the residual sulfate concentrations were lower than the other persulfate activation methods evaluated (matrix, iron and base activation).

Using the treatability results Geosyntec designed and conducted a large-scale field pilot test at the Middlefield-Ellis-Whisman Superfund Site in California, USA. The target injection zone is a heterogeneous mix of dense clays and sands. The site-specific design involved injecting

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314,000 liters of oxidant solution (3,200 kgs of sodium permanganate and 9,300 kgs of sodium persulfate in total) over a period of 3 weeks via injection wells and direct push methods. Observed reductions in contaminant mass have been greater than 90 % compared to baseline concentrations as shown in the graph below.

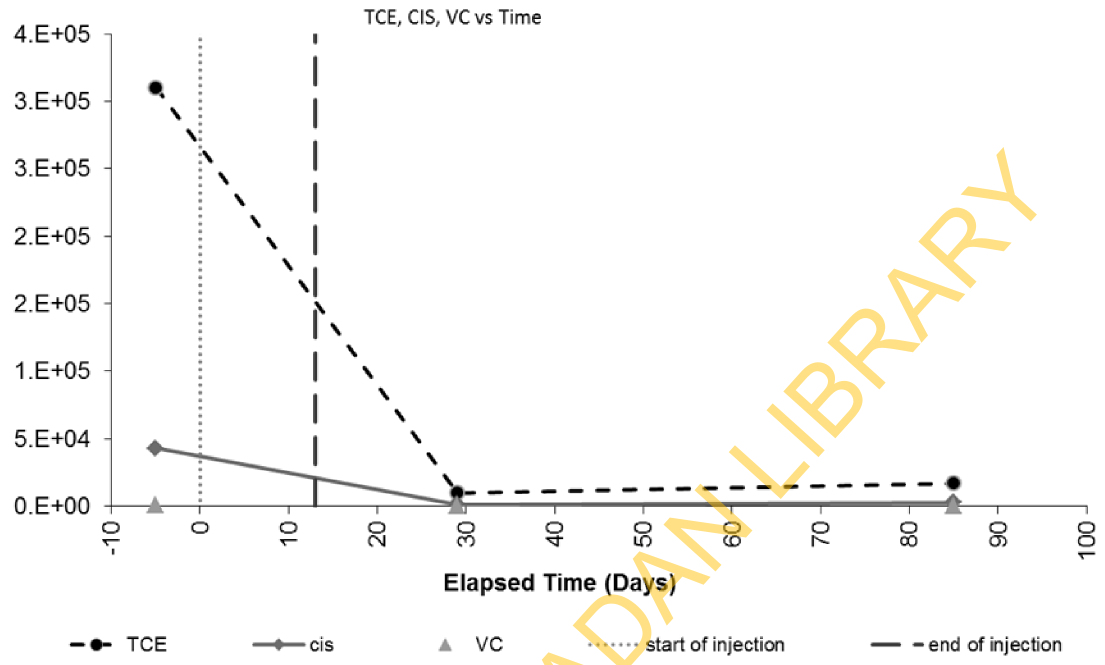

Fig. 1. Compares the post first injection TCE, CIS and VC 73 days post-injection to baseline concentrations.

CONCLUSIONS

The use of a combination of permanganate and persulfate was identified in Patent No. 6019548; although the purpose of the permanganate addition identified was not MnAP. Therefore, the combination of permanganate and persulfate has not been widely explored or utilized in the field. This treatability assessment and pilot study has demonstrated that MnAP is is an innovative activation method and aggressive in situ chemical oxidation remedial tool. Another significant benefit are the associated cost benefits to using the combined oxidative approach over the traditional permanganate application for the treatment of chlorinated volatile organic compounds such as TCE and that is significant cost savings of this engineered dual oxidant approach.

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URBAN RENEWAL: PREPARING FOR A JOURNEY NOT PACKING FOR A DESTINATION

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INTRODUCTION

The world population is growing. Real Estate specialists, Frank Knight, suggest that the urban population will grow by some 1.1million before 2030 – equivalent to the population of India (Frank Knight, 2015). They identify three factors that will drive the growth of cities. The second is “Former-industrial areas transform[ed] into new districts, bringing offices, leisure & homes closer together.”

The, growing, world is going to the beach – urbanisation continues apace and mostly in the coastal zone. Mankind has long lived by the sea. However many littoral urban areas associated with major port facilities, industry and refining now lie abandoned and underused. Such areas are often close to the centre of economic and social gravity of a city. As such, urban growth that can happen in these under employed quarters can prevent sprawl, increase resource efficiency and create places where social and intellectual capital can be created. However I am not convinced re*new*al is necessarily the most appropriate word to describe the process of bringing such land back into beneficial use.

COASTAL CITIES

Australia perfectly, but unsurprisingly, illustrates this paralic paradigm. Its five cities with populations over 1 million (Sydney, Melbourne, Brisbane, Perth and Adelaide) comprise some 63% of the country’s population. Canberra, some 1.8% of the total population, is the inland exception.

Globally, 8 of the top 10 cities in the ATKearney index, ranking 84 cities based on how globally engaged they are, are on the coast. The remaining two are Beijing and Chicago, on the shore of lake Michigan.

During the 3rd Global Soil Week, held in Berlin in April 2015, a workshop on the soil-sea nexus was organised by representatives of the EU Joint Research Centre, Germany’s IASS and INSPIRACTION, a new European Union funded Horizon 2020 project. The younger (roughly under 35 years old) participants in the World Café$^{\text{TM}}$ part of the workshop often referred to the need to honour and reflect history and culture in urban redevelopment projects. This sense of place is hard to define but easy to lament. The smell of the sea breeze, the sound of gulls, the sight of small boats returning to a safe haven. The ruins of ancient fortifications; the sturdy masonry buildings of former administrations; the statues or monuments to enduring personalities or memorable events. Imagine your favourite sea side café or bar and then delete all of the above.

*RE*MIND ME WHAT WE DO!

Our sector is in the soil and groundwater remediation and land reclamation business. We contribute to ecological restoration; re-use of aggregate, recovery of materials. We work alongside those who refurbish buildings and restore structures. The purpose is to redevelop buildings and spaces that will help regenerate economies and thereby revive and revitalise communities. Occasionally after a terrible natural or manmade disaster we have to rebuild and renew from scratch. Mainly however we progress incrementally from what was there already. However *r*epetition is not an option. We need to build new tomorrows to serve different purposes and to do so in new ways.

URBAN TOMORROWS

Confucius observed “I hear and I forget. I see and I remember. I do and I understand.” Alfred Einstein advised “Look deep into nature, and then you will understand everything better.”

There is no reason to doubt the wisdom of both statements. However action before understanding is not really an option when it comes to redeploying urban areas. The “consume and discard” or “consume, set aside and perhaps return to at some point in time” approaches to urban land management are neither acceptable nor sensible. A “consume and redeploy” approach that ensures land is in use or being prepared for its next use is needed.

SYSTEMS

Aristotle realised that “the whole is more than the sum of its parts”. Cities are wholes made up of many parts. Cities are complex complexes of natural and man-made sub-systems that interact with each other and the city’s hinterland. These interactions need to be understood and the consequences of any changes, such as urban renewal, need to be predicted and accepted before action is taken. Collateral damage or unintended consequences are increasingly unacceptable in urban land management. However when one is dealing with systems as complex as cities seem to be, we face perhaps intractable challenges. Einstein, unsurprisingly, had got there first: “When the number of factors coming into play in a phenomenological complex is too large scientific method in most cases fails. One need only think of the weather, in which case the prediction even for a few days ahead is impossible.”

CONCLUSIONS

Urban renewal *senso lato* is possible. Barcelona, Glasgow and Lille have managed a transition akin to a rebirth. But renewal is not inevitable. Liverpool, Detroit and Ordos are reminders that sometimes the impossible is just that… or at least out of reach for now.

Vision, planning and ever-deepening understanding of the social, environmental and economic dimensions of a place are essential. To this must be overlain and integrated understanding of governance, communications and technology.

In English law, public bodies’ decisions can be judged in a court of law. The outcomes of judicial reviews revolve, not around if the decisions were right or wrong, but instead around whether the decision was a reasonable one.

It is nigh on impossible to know whether a decision made today will be judged in 25, 50 or even 100 years’ time as the right one. The best we can expect is that it will have been found reasonable given what was or ought to have been known at the time.

REFERENCES

ATKearney (2014) Global Cities, Present and Future. http://www.knightfrank.com/global-cities-index-2015/articles/global-cities accessed 6 May 2015

Frank Knight (2015) Global Cities: The 2015 Report. http://www.knightfrank.com/global-cities-index-2015/articles/global-cities accessed 6 May 2015

Nathanail, C.P. and Ashmore, M.A. (2014). Integrated Framework for systematic evaluation of brownfield regeneration. FP7 HOMBRE project deliverable D6.2 Available from http://www.zerobrownfields.eu/HombreTrainingGallery/HOMBRE_D6.2_final.pdf accessed 9 May 2015

MODELS AND LESSONS FOR DEVELOPING A CONTAMINATED SITE PROGRAM: AN INTERNATIONAL REVIEW

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INTRODUCTION

Contaminated sites associated with economic growth and increased urbanization pose growing public health, environmental, economic, and political problems, particularly for low and middle income countries. Experience in countries with contaminated site programs has shown that the complexity and cost of remediation and restoration of sites only grows with time. While a number of European, North American, and several Asia Pacific countries have decades of experience with such programs, other countries are just beginning to face this issue as their economies and environmental programs mature. They may benefit from the wealth of experience derived from implementing such programs elsewhere in the world.

BACKGROUND

This presentation reviews the findings of two recent World Bank reports: “Developing a Program for Contaminated Site Management for Low and Middle Income Countries” which offers approaches for developing a contaminated site program at the national level and “Financing Mechanisms for Addressing Remediation of Site Contamination” which describes various financing mechanisms that can support such a program. Each report draws information from countries around the world that have developed programs and have experience with different financial approaches for remediation of sites. Neither report is normative, but each offers a range of options for approaching the major issues that arise in contaminated site program. Extensive references for further information are included in both.

Findings: Developing a Program for Contaminated Site Management

This report describes several major dimensions to consider in developing a program as well as recommendations for moving forward with implementation.

Policy and legislation

First, at the broad policy level, there are alternative approaches to embracing contaminated land as either a soil pollution initiative (alongside air and water pollution control, for example) or as a soil protection initiative that embraces sustainability in rural and urban contexts, taking into account agricultural, mining, industrial, and other sectors. Second, legislation needs to be considered in the context of water, waste, groundwater, and other existing statutes being mindful of several cross-cutting principles that seem to be foundational for successful programs. Some countries have chosen to build upon existing statutes, while others have chosen to create separate legislative authority. In either case, there are some common principles that often underlay any approach. They include: prevention, “polluter pays” principle, an effective liability regime, a risk based clean-up approach, sustainable use of land, and transparency of information, as well as recognition of several funding approaches.

Regulatory issues

Matters requiring regulatory action constitute a third tier of decision-making in developing a contaminated site program; there are alternative approaches for at least four broad issues. First among these is defining the focus on the program, including its initial and continuing priorities. This issue deals with the variety of options to creating a listing or inventory of sites (including the types and kinds of sites included as well as the levels of contamination that are of concern), whether it is comprehensive or focused on current work, and a variety of other parameters. Defining the pace and scale of development of the program is a second important topic in terms of initial environmental, legislative, and political goals as well as available financial and personnel resources at various levels of government. While there is much consensus among countries in defining the steps in the process from discovering and investigating sites through their cleanup and (possibly) continued long-term oversight, there are also many nuances to this third major issue as to the level of resources and types of information needed for each step. A final regulatory issue involves establishing each step in the site discovery through clean-up process and roles played by government and the private sector (site owners and consultants). Financing a contaminated site program, especially if it involves redevelopment of former industrial/abandoned sites (also called brownfields), may require unique special arrangements that permit public private partnerships.

Organization and implementation

Illustrative organization functions for governments are given in the report with special emphasis on management accountability and performance measurement, information and records management, quality assurance, aspects of external affairs (including community involvement and intergovernmental relations) and monitoring the state of the practice. Issues related to implementation are framed in terms of short and longer terms actions that can be taken (including pilot projects) and a national management plan for contaminated sites is highlighted as a multi-purpose document that can not only frame and summarize issues, but also serve as a road map for action that is useful to many stakeholders.

Findings: Financing Remediation of Sites

This report describes five established mechanisms and several emerging approaches used by governments and the private sector to finance the remediation of contaminated sites. Drawn from examples in at least six countries, a basic overview of the financing tool is offered including identifying underlying economic and legal conditions that must be in place prior to creating a program to address contaminated site remediation. Following the overview, there is a discussion on how the mechanism can be implemented and administered to greatest effect. Most of the approaches are implemented at the local, municipal, or state level, but each requires tax, banking and finance infrastructure that are supported or defined at the national level—often consistent with existing practice in real estate, banking, and municipal finance. Case studies of existing programs illustrate how concepts can be adapted to diverse situations. There is an analysis of the relative strengths/opportunities and weaknesses/ limitations presented by each financing mechanism and a discussion of its potential to address contaminated sites globally.

Five principal financing tools

Bond programs (i.e. a loan with the entity issuing the bonds on the capital markets in return for cash) constitute a familiar and traditional approach for supporting the costs of site cleanup. Both government bonds and private activity bonds have emerged as approaches for site remediation. A second mechanism, revolving loan funds (i.e. a self-replenishing pool of money, utilizing interest and principal payments on active loans to issue new loans), can be structured for partial or complete debt forgiveness—if certain criteria are met. In addition, communities may offer indirect enhancements to projects needing a private loan, such as collateral support, loan loss reserves, or guarantees, to mitigate the weaknesses perceived by private financial institutions. A third mechanism, tax Increment and special assessment financing, is a tool that allows local governments to invest in infrastructure and other improvements and pay for them by capturing the increase in property tax revenues generated by the enhancements. Tax credits and incentives are the fourth mechanism and involve a monetary reduction of a taxpayer's tax liability. (This is different from a tax deduction, which is a reduction of a taxpayer's income subject to tax, on which the taxpayer's ultimate tax liability will be determined.). Grant programs constitutes the fifth tool used to finance site remediation; while requiring no payback to the granting organization, sometimes "clawback" provisions are included in grant requirements to assure that certain conditions or social goals are met. Several new approaches are being piloted in various countries

REFERENCES

Kovalick, W. and Montgomery, R. (2014) Developing a Program for Contaminated Site Management for Low and Middle Income Countries. World Bank, Washington, D.C. 51p.

Council of Development Finance Agencies (2014) Financing Mechanisms for Addressing Remediation of Site Contamination. World Bank, Washington, D.C 77p.

FISHERMANS BEND URBAN RENEWAL AREA: PROACTIVE GROUNDWATER BACKGROUND STUDIES

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INTRODUCTION

This presentation will discuss how Victorian State Government agencies are proactively collaborating to address potential environmental constraints in the development of the Fisherman's Bend Urban Renewal Area (FBURA).

Brownfields urban redevelopment is a very topical subject that responds to the sustainability and infrastructure pressures that increased population and expanding metropolitan areas pose to a society.

Fishermans Bend Urban Renewal Area (FBURA) is a precinct of 240 hectares in size and has a projected development timeframe of over 40 years. The objective is a mixed use precinct with significantly increased population through new medium to high density residential sub-precincts.

In Victoria, where land changes from an industrial or commercial use into residential use, the planning system has safeguards to ensure the future use is safe for future residents. The system, however, is largely based on title boundaries and was not designed for large scale, long term redevelopment projects like FBURA.

A key consideration will be the potential for land and groundwater contamination across the site as a result of the historical industrial practices and historical unregulated filling of the site during its initial development.

If environmental constraints, in particular in relation to groundwater, are better understood then a safe and effective transformation of the area will follow.

METHODS

EPA and the Metropolitan Planning Authority identified that a proactive approach to understand the regional background conditions of groundwater in the area would enable safer environmental outcomes and clearer, faster regulatory and planning processes.

EPA, in collaboration with MPA, called for a $350,000 tender relating to assessment of groundwater quality at Fishermans Bend.

The work will involve a combination of desktop site history reviews, drilling of new groundwater observation bores and extensive sampling and analysis.

This work will complement earlier geotechnical studies of Fishermans Bend undertaken during the development of the Fishermans Bend Strategic Framework Plan.

The groundwater project will allow EPA and planning agencies to advise developers on aspects that will require attention. It will also further inform the Metropolitan Planning Authority's review of the Strategic Framework Plan.

A total of sixteen submissions from environmental consultants were received and a contract was signed for the work on 5 June, 2015. All works are planned to be finished by 30 December 2015.

The project will support EPA and MPA statutory decisions by providing:

- Advice about which beneficial uses of groundwater apply and what regulatory tool may be used by EPA;
- Guidance for environmental auditors and developers on suitable risk management approaches (engineering and building controls);
- Advise the MPA on how individual sites should assess and address “hotspot” contamination to mitigate risks to human health and the environment (where identified); and
- Consistent approach for referral of Fishermans Bend planning applications.

RESULTS AND DISCUSSION

The desktop review process has been completed. Existing groundwater observation wells are being considered to determine whether they can complement the planned drilling program. The final drilling program and suite of analytes will be presented at the conference.

CONCLUSIONS

EPA and MPA are displaying the responsive and innovative nature to deliver together public value in the form of safer, clearer and faster regulatory and planning processes. Depending on outcomes, this approach may be applicable to other sites.

REFERENCES

MPA 2014, Fishermans Bend Strategic Framework Plan.

COMMUNITY CONSULTATION IN AN URBAN RENEWAL PROJECT AND COMPETING OBJECTIVES

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INTRODUCTION

With Australia being one of the most highly urbanised societies in the world and population growth placing increasing pressure on the demand for housing, urban renewal is seen as a key component. According to projections from the Australian Bureau of Statistics and the Department of the Treasury (Australia) it is anticipated that Australia's population will continue growing and will reach 35 million by 2050. It is estimated that 72% of this growth will occur in our cities. In addition, demographic changes, including aging population and an increase in smaller households, is leading to a greater demand in urban planning for housing and also different types of housing overall.

Urban renewal and consolidation is changing the character of Australian cities. Planning strategies have focused on containing the outward physical sprawl of cities, redeveloping the inner city and older zones and, particularly disused industrial and commercial spaces into new residential spaces.

These older industrial and commercial areas often come with contamination legacies. In order to ensure that the sites are suitable for their new residential use (and associated public spaces), a contaminated site audit is often a requirement of development approval. However, often the contamination is easier to manage than multiple stakeholders.

The Western Australian Department of Environment Regulation (DER) notes that “community engagement is an integral part of contaminated site assessment and remediation” (DER, 2014). So how do you ensure that the community consultation covers all interested parties involved in an inner city urban renewal project? What happens when the parties have differing objectives and agendas?

DISCUSSION

DER requires more extensive community engagement for sites that pose a significant risk to human health, the environment or environmental values; sites that are affecting adjacent land or where the contamination has the potential to migrate off site or affect sensitive off-site receptors. The scope and detail of community engagement also depends on the size of the project and the level of community interest or concern.

During a recent contaminated site audit, the assessment consultant easily identified the relevant stakeholders. Local council, Swan River Trust, DER, adjacent school and service providers. Then add the site owner and their project manager, pre-construction contractors, future developer and their consultants, media and state government ministers. There could also be others such as community groups and recreational users that should have been added to the list.

How and when to “engage” with each group varied dramatically, but generally fell into one of three categories.

(a) Inform frequently
(b) Inform occasionally
(c) React

Most community engagement fell into the last two categories – inform occasionally or react. While this method saw the project going “full steam ahead” during the initial stages of assessment, delays at the tail end of the project were noticeable as the parties became sceptical or did not want to otherwise endorse reports or management measures. In some cases, the reluctance to endorse reports or actions that had already been undertaken appeared to be related to financial and/or contractual issues, not just on environmental matters.

CONCLUSIONS

The site was successfully reclassified by the DER in July 2014 and noted to be suitable for the redevelopment, paving way for the construction of apartments, shops, cafes, bars and public spaces, the first of which are due to be completed in late 2015. However, the implications of the somewhat ineffective community consultation process are having flow on effects for other projects resulting in higher levels of concern and involvement by some of the interested parties.

REFERENCES

Department of Environment Regulation (2014) *Assessment and Management of Contaminated Sites*.

POTENTIAL HEALTH IMPACTS OF TOXIC CHEMICALS IN FISH: THE CASE OF PEARL RIVER DELTA, SOUTH CHINA

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INTRODUCTION

Food safety is any action and policy which ensure food is safe, in the entire food chain, i.e. from production to consumption (WHO, 2013). In fact, “chemical food contaminants” is one of the 3 key global food safety concerns. The other two are “spread of microbiological hazards”, and “assessments of new food technologies (e.g. genetically modified food). Food safety is currently one of the major public health issues in the world.

METHODS

The present paper attempts to review the information concerning various pollutants detected in farmed fish produced in the Pearl River Delta (PRD), the most developed region in China, and their possible associations with body loadings of these chemicals (through analyses of various human tissues) and their potential health effects, by citing local and regional examples.

RESULTS AND DISCUSSION

The Pearl River Delta (PRD): Environmental contamination and fish farming

Being the most developed region in China, PRD has transformed to the world centre for manufacturing electronic/electrical equipment, in addition to its active mining industries. These together with overuse/abuse of antibiotics and pharmaceutical products, a wide range of toxic chemicals are finding their way to food production systems (Liu & Wong, 2013; Zhao et al, 2012). Most of the fish consumed in PRD are farmed fish, which are highly susceptible to these toxic chemicals discharged nearby. Seaborne plastic residues commonly found in near-shore environment may act as magnets that absorb toxic chemicals, and subsequently transfer to fish. Feeding farmed fish with contaminated trash fish and fishmeal (commonly derived from trash fish) will also contribute to adverse health effects. In addition, speciation of chemicals emitted, e.g. mercury (Hg) derived from coal combustion reaching sediment beneath mariculture rafts (with higher organic matter) may be transformed by sulphide bacteria to organic Hg (i.e. methyl Hg), which is highly toxic (Liang et al, 2011).

Health impacts due to food contamination

Common health problems such as cancers (arsenic, asbestos, dioxins), neurological damage and lower IQ (lead, arsenic, Hg), kidney disease (Hg, lead, cadmium), and skeletal and bone diseases (lead, fluoride, cadmium) are serious issues in developing countries (Bouwman et al, 2012). In particular, there seems to be data gap concerning emerging chemicals of concern (e.g. phthalates) in rapid developing countries (Wong et al, 2012).

It has been noted that the sub-fertile male in Hong Kong, with higher hair Hg concentrations are associated with their higher fish consumption rates (Dickman et al, 1998). Ko et al, 2013) indicated the potential linkage with high levels of Hg and cadmium in autistic children from coastal populations, possibly through oral intake of fish and shellfish; whereas high levels of arsenic and lead in inland populations, due to environmental pollution. Higher Hg levels detected in blood plasma of Hong Kong general public (based on samples donated by Red Cross) (Liang et al, 2013), and in the hair of residents of fish farming villages in PRD (Shao et al, 2013) may reflect their higher rates of seafood consumption. Furthermore, it has been revealed that patients with uterine leiomyomas contained higher concentrations of persistent organic pollutants (POPs) and heavy metals in their adipose tissues, linking with their seafood diet (Qin et al, 2010).

In addition, uncontrolled recycling of electronic wastes (e-waste) also emitted a wide range of toxic chemicals. High body loadings of different toxic chemicals (notably flame retardants) of workers and residents of two major e-waste recycling sites (Guiyu and Taizhou) in China, are associated with their dietary intakes (Chan et al, 2007; Leung et al, 2007; Wong et al, 2007). There seemed to be an abrupt increase of major diseases (such as respiratory system), according to the limited data provided by a local hospital at Taizhou.

CONCLUSION

In order to better manage toxic chemicals, especially those commonly found in food items (Qin et al, 2011; Tsang et al, 2009), there seems to be an urgent need to establish a regional list of these toxic chemicals, paying attention to their sources, fates and environmental and health effects, based on specific regional conditions (Wong et al, 2012). In addition, the practice of "green aquaculture" is necessary to ensure quality and safe aquatic products.

REFERENCES

Bouwman H, MH Wong, R Barra (2012). GEF Guidance on Emerging Chemicals Management Issues in Developing Countries and Countries with Economy in Transition. UNEP/GEF.

Chan JKY, GH Xing, Y Yu, Y Liang, LX Chen, SC Wu, CKC Wong, CKM Leung, MH Wong (2007). Body loadings and health risk assessment of PCDD/Fs at an intensive electronic waste recycling site in China. Environ Sci Technol 41: 7668-74.

Dickman MD, CKM Leung, Leong MKH (1998). Hong Kong male subfertility links to mercury in human hair and fish. Sci Tot Environ 214: 165-174.

Ko LYY, YY Qin, MH Wong (2012). Heavy metal overloads and autism in children from mainland China and Hong Kong: a preliminary study. In: Environmental Contamination – Health Risks and Ecological Restoration. Wong MH (Ed). Taylor & Francis/CRC, London.

Leung AOW, WJ Luksemburg, AS Wong, MH Wong (2007). Spatial distribution of PBDEs and PCDD/Fs in soil and combusted residue at Guiyu, an e-waste recycling site in SE China. Environ Sci Technol 41: 2730-7.

Liang P, DD Shao, SC Wu, JB Shi, FY Wu, SCL Lo, WX Wang, MH Wong (2011). The influence of mariculture on mercury distribution in sediments and fish around Hong Kong and adjacent mainland China waters. Chemosphere 82: 1038-43.

Liang P, YY Qin, C Zhang, J Zhang, YC Cao, SC Wu, CKC Wong, MH Wong (2013). Plasma Hg levels in HK residents: In relation to fish consumption. Sci Total Environ 463-464:1225-9.

Liu JL, MH Wong (2013) Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China. Environ Intl 59: 208-24.

Qin YY, CKM Leung, AOW Leung, SC Wu, JS Zheng, MH Wong (2010). Persistent organic pollutants & heavy metals in adipose tissues of patients with uterine leiomyomas and the association of these pollutants with seafood diet, BMI, & age. Environ Sci Pollut R 17: 229-40.

Qin YY, CKM Leung, AOW Leung, JS Zheng, MH Wong (2011). Persistent organic pollutants in food items collected in Hong Kong. Chemosphere 82: 1329-36.

Shao DD, Y Kang, Z Cheng, HS Wang, MJ Huang, SC Wu, KC Chen, MH Wong (2013). Hair Hg levels and food consumption in residents from PRD, South China. Food Chem 136: 682-8.

WHO (2013). Ensuring food safety and nutrition security to protect consumer health: 50 years of the Codex Alimentarius Commission. Bull World Health Organ 91: 468-468A.

Wong MH, SC Wu, WJ Deng, XZ Yu, Q Luo, AOW Leung, CSC Wong, WJ Lukesmburg, AS Wong (2007). Export of toxic chemicals – A review of the case of uncontrolled e-waste recycling. Environ Pollut 149:131-40.

Wong MH, MA Armour, R Naidu, M Man (2012). Persistent toxic substances: sources, fates and effects. Rev Environ Health 27: 207-13.

Tsang HL, SC Wu, CKC Wong, CKM Leung, S Tao, MH Wong (2009). Risk assessment of PCDD/Fs levels in human tissues related to major food items based on chemical analyses and micro-EROD assay. Environ Intl 35: 1040-7.

Zhao YG, CKC Wong, MH Wong (2012). Environmental contamination, human exposure and body loadings of PFOS, focusing on Asian countries. Chemosphere 89: 355-68.

USING A LIFETIME PHYSIOLOGICALLY BASED PHARMACOKINETIC MODEL TO ESTABLISH ARSENIC DRINKING WATER GUIDANCE

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INTRODUCTION

Human exposure to Arsenic (As) has been a worldwide concern and drinking water is considered as a significant pathway. World Health Organization (WHO) guidance for drinking water is 10 ug/L. However, such guidance was estimated based on practical difficulties in removing arsenic from drinking-water, rather than human health risk assessment (WHO, 2011). To establish the guidance based on risk assessment requires dose-response curve, as well as the source allocation for drinking water.

Several studies have demonstrated the association between As exposure and potential human health risk. However, all existing dose response curves were based on external exposure concentration. Growing evidence shows that risk increases with the duration of exposure. Thus, to include duration of exposure in the linkage between exposure and risk requires application of lifetime toxicokientic model, which is unavailable from previous studies. Meanwhile, to calculate the source allocation for drinking water requires a national exposure assessment survey.

The aim of this study is to develop drinking water guidance for As. Specifically, the objectives include: using 1) data from total diet studies for exposure assessment and 2) biomonitoring data from National Health and Nutrition Examination Survey (NHANES) to develop lifetime physiologically based pharmacokinetic (PBPK) model. The study presented here is science underpinning in the management of arsenic.

METHODS

This study consisted of four steps: 1) the inclusion of data on ingestion (fc) and arsenic concentration, was retrieved from total diet studies (2006-2011) to estimate daily As uptake; 2) urinary As information from NHANES (2011 – 2012) was analysed, and this biomonitoring data was applied for development of lifetime PBPK model; 3) the data regarding dose and exposure time was converted to cumulative urinary concentration by using the established lifetime PBPK model (established in step 2), and then the logistic model was employed to link cumulative urinary arsenic and risk. The epidemiological study regarding the skin lesions (hyperpigment and keratosis) and arsenic exposure in India was selected as data source; 4) based on acceptable risk level, the drinking water guidance was developed.

RESULTS AND DISCUSSION

The total diet daily intake (median value) was estimated to be 0.22 µg/kg bw, and that value for inorganic fraction was estimated to be 0.028 µg/kg bw. As shown in Figure 2, organic As contributed nearly 90% to total As, which was much higher than allocation from inorganic As. The reason is seafood contributed largest to total As exposure, while most As speciation in seafood is organic in nature. On the other hand, the allocation from bread and rice for inorganic As was the highest, followed by the drinking water and fish.

The initial parameters for lifetime PBPK model were collected from previous models, and the sensitivity parameters were adjusted in this study. The huge decrease in the residual errors has validated the PBPK model. Then, the developed logistic functions for hyperpigment and keratosis were showed in Figure 3. Setting 5% extra risk as acceptable risk level, the drinking water guidance was calculated to be 3 μg/L.

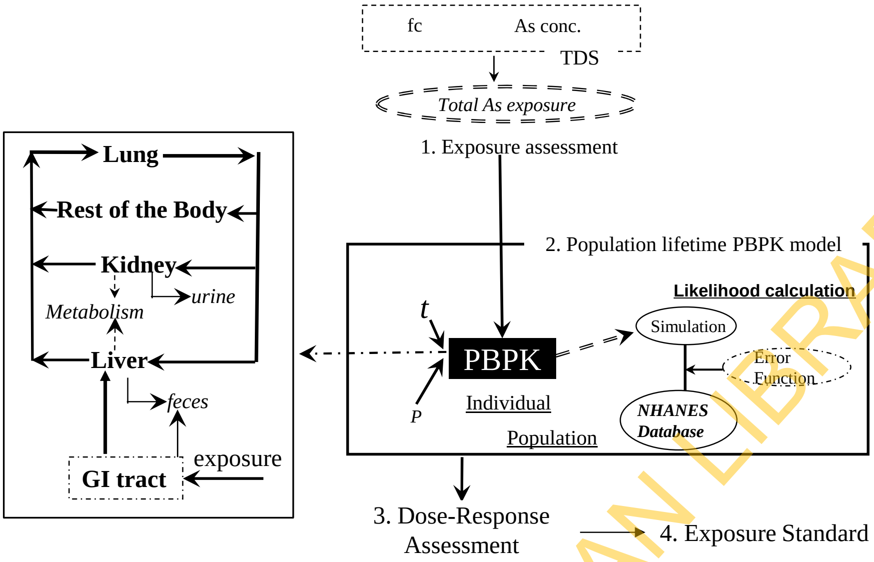

Fig.1. The framework to establish drinking water guidance for arsenic

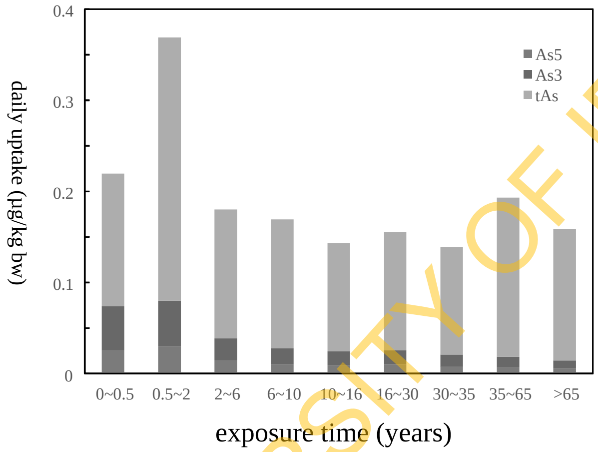

Fig.2. The daily arsenic exposure for different arsenic speciation, based on various exposure time groups;

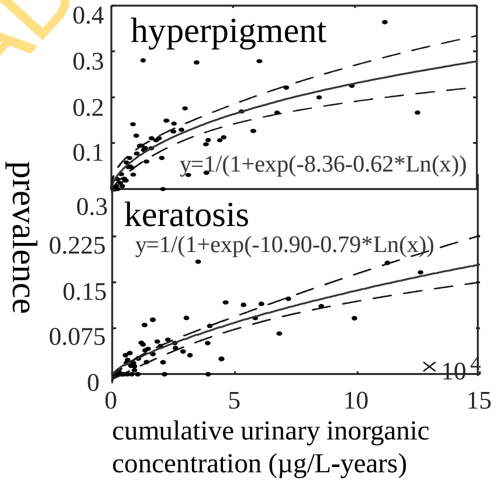

Fig. 3. The linkage between cumulative urinary inorganic concentration and risk

CONCLUSION

The new established drinking water guidance is approximately 60% lower than WHO guidance, which suggests current guidance probably results in high human risk.

DATA SOURCE

TDS: http://www.fda.gov/Food/FoodScienceResearch/TotalDietStudy/ucm184293.htm
NHANES: http://wwwn.cdc.gov/nchs/nhanes/search/nhanes11_12.aspx
PBPK initial parameters: 1) Regul Toxicol Pharmacol; 29(part 1 in 2):128–141;
2) J Pharmacokinet Pharma; 35(1) 31-68.

REFERENCE

WHO, 2011, Guidelines for drinking-water quality, fourth edition. Available: http://www.who.int/water_sanitation_health/publications/dwq_guidelines/en/

SOURCES, SPECIATION AND BIOAVAILABILITY OF HEAVY METAL(LOID)S IN COMPLEMENTARY MEDICINES

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INTRODUCTION

Complementary medicines are also known as traditional, natural or alternative medicines, and include herbal medicines, vitamin and dietary health supplements, and traditional Ayurvedic, Chinese and homoeopathic medicines (WHO 2005). Globally, self-prescribed vitamins, herbal medicines and mineral supplements are the most common Complementary medicines used. Although the intention of using Complementary medicines is to gain health benefits, there is limited evidence of the efficacy of these medicines and the risks due to contamination (Harvey et al. 2008). The risks from contaminants include pesticide residues and toxic heavy metal(loid)s such as cadmium, arsenic, lead and mercury (Denholm 2011).
These heavy metal(loid)s reach Complementary medicines during the cultivation of plants used for these medicines, accidental cross-contamination occurring during processing, and the introduction of heavy metal(loid)s as a therapeutic ingredient (Saper et al. 2004; Sarma et al. 2011).

The overall objective of this study is to examine the speciation and bioavailability of heavy metal(loid)s in selected Complementary medicines. The main hypothesis of this research is that the bioavailability of heavy metal(loid)s in complementary medicines relates to their speciation.

METHODS

Twelve complementary medicines including 6 each Herbal and Ayurvedic medicines were used in this study. The samples were analysed for: (i) total heavy metal(loid) contents including arsenic, cadmium, lead and mercury; (ii) speciation of heavy metal(loid)s using a sequential fraction technique; and (iii) bioavailability of heavy metal(loid)s using a physiologically-based *in vitro* extraction test (PBET) (Sanderson et al. 2012). The daily intake of heavy metal(loid)s through the uptake of these Complementary medicines as measured by total, soluble and bioavailable metal(loid) contents was compared with the safety guidelines for these metal(loid)s (Jayawardene et al. 2010).

RESULTS AND DISCUSSION

The results indicated that the heavy metal(loid)s content varied between the metal(loid) species and Complementary medicines. Generally Ayurvedic medicines contained higher levels of As, Cd, Hg and Pb than Herbal medicines and the amount of Pb was much higher than other 3 metal(loid)s.

The sequential fractionation study indicated that while organic-bound metal(loid) species dominated the Herbal medicines, inorganic bound-metal(loid) species including oxide-bound and carbonate bound dominated the Ayurvedic medicines. Both soluble and residual fractions contributed a small proportion to the total metal(loid) contents both in Herbal and Ayurvedic medicines. This indicates that in the case of Herbal medicines most of the heavy metal(loid)s are derived from plant uptake, whereas in the case of Ayurvedic medicines these heavy metal(loid)s are derived from inorganic mineral input.

The PBET data indicate that bioavailability varied between heavy metal(loid)s and also between Herbal and Ayurvedic medicines. In general bioavailability as a percentage of total metal(loid) content followed: As > Cd > Hg > Pb, and was higher in Ayurvedic than Herbal medicines. This indicates that heavy metal(loid)s added as a mineral therapeutic input are more bioavailable than those derived from plant uptake. There was a positive relationship between soluble metal(loid) fraction and bioavailability indicating that solubility is an important factor controlling bioavailability of heavy metal(loid)s in complementary medicines.

The daily As intake values as estimated by total, soluble and bioavailable metal(loid) contents are unlikely to exceed the safe threshold level for both Herbal and Ayurvedic medicines. However, the daily intake values for Cd, Hg and Pb as estimated by total and bioavailable metal(loid) contents are likely to exceed the safe threshold level in some of the Ayurvedic medicines.

CONCLUSIONS

This research demonstrated that complementary medicines:

(a) contain significant levels of toxic heavy metal(loid)s such as As, Cd, Pb and Hg which are bioavailable;

(b) the bioavailability of the heavy metal(loid)s in these medicines correlate well to the soluble fraction of the respective metal(loid)s and thus soluble fractions could be used in the future to predict bioavailability; and

(c) heavy metal(loid) toxicity is likely to result from long-term exposure to these toxic substances from the regular intake of these medicines and this requires further investigation.

REFERENCES

Denholm, J. (2011) Complementary medicine and heavy metal toxicity in Australia, viewed 12 March 2014, http://www.webmedcnetral.com.

Harvey, K.J., Korczak, V.S., Marron, L.J. and Newgreen, D.W. (2008) Commercialism, choice and consumer protection: regulation of complementary medicines in Australia. *Medical Journal of Australia* 188:21–25.

Jayawardene, I., Saper, R., Lupoli, N., Sehgal, A., Wrightab, R.O. and Amarasiriwardena, C. (2010) Determination of in vitro bioaccessibility of Pb, As, Cd and Hg in selected traditional Indian medicines. *J. Anal. At. Spectrom*, 25:1275–1282.

Sanderson, P., Naidu, R., Bowman, M. and McLure, S. (2012) Effect of soil type on distribution and bioaccessibility of metal contaminants in shooting range soils. *Science of Total Environment,* 438:452-462.

Saper, R.B., Kales, S.N., Paquin, J., Burns, M.J., Eisenberg, D.M., Davis, R.B. and Phillips, R.S. (2004). Heavy metal content of Ayurvedic herbal medicine products. *Journal of the American Medical Association,* 292:2868–2873.

Sarma, H., Deka, S., Deka, H., Saikia, R. and Whitacre, D. (2011). Accumulation of Heavy Metal(loid)s in Selected Medicinal Plants. *Reviews of Environmental Contamination and Toxicology,* 214: 63-86.

WHO (2005). *National policy on traditional medicine and regulation of herbal medicines: Report of a WHO global survey*, World Health Organization, Geneva.

CONCENTRATION OF ARSENIC IN HOME GROWN VEGETABLES: HEALTH IMPLICATIONS

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ABSTRACT

Dietary exposure of arsenic (As) is a matter of concern for human health from the consumption of home grown vegetables. This study reports concentrations of As in vegetables in an As-contaminated area (Noakhali) of Bangladesh and daily intake from this source. The mean concentration of total As in vegetables was 113 µg kg^{-1} and As speciation shows that on an average 87% of total As were present as inorganic As. The daily estimated average As intake from different vegetables ranged between 3 to 36 µg kg^{-1}. This study reveals that high percentage of As consumption from vegetables poses at risk to the study population.

INTRODUCTION

Geogenic arsenic (As) contamination of groundwater was reported in various regions worldwide, particularly in countries of Southeast Asian regions. Bangladesh and West Bengal state of India are the two worst As-contaminated areas where more than 100 million people are potentially at risk from groundwater As contamination (Rahman et al. 2009a). Several articles have already been reported on the accumulation of As in food crops especially rice and vegetables grown in As-contaminated areas of Bangladesh (Alam et al. 2003; Das et al. 2004; Williams et al. 2006; Smith et al. 2006; Rahman et al. 2009). However, it is still essential to determine the content of As in home grown vegetables in As-contaminated areas of Bangladesh. The main objective of this study was to determine the quantity of As ingested by adults from home grown vegetables by the local population and to estimate the risk posed by the consumption of contaminated vegetables.

METHODS

A total of 87 home grown leafy (n=62) and non-leafy (n=25) vegetable samples were collected from 14 families in two adjacent villages (Chiladi and Basantapur) of Noakhali district in Bangladesh during December 2008. A few samples (n=5) of cooked vegetables were also collected Standard protocols were used to wash, dry and digestion of the vegetables samples. as of Rahman et al. (2009b). An Agilent 7500c inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of As in vegetables.

RESULTS AND DISCUSSION

The vegetables with the highest mean As levels were as follows: arum leaf>pumpkin leaf>Coriander leaf>radish leaf>gourd leaf>radish>spinach>red amaranth>arum stem>Indian spinach>arum tuber>bean>papaya>green chilli>eggplant. The result shows that the mean and median As concentrations in all vegetables were 113 µg kg^{-1} and 90 µg kg^{-1}, respectively, with a range from 11 to 464 µg kg^{-1} (dry weight). The maximum As concentration was observed in a sample of gourd leaf (464 µg kg^{-1}). In case of leafy and non-leafy vegetables, the average As concentrations were 141 µg kg^{-1} and 45 µg kg^{-1}, respectively. Thus, As content in leafy vegetables was 3 times higher than non-leafy vegetables. The range of As in this study was comparable with Alam et al. (2003) but much lower than the studies of Das et al. (2004) and Williams et al. (2006).

In case of leafy vegetables, the mean and median As concentrations were 141 µg/kg and 110 µg/kg, respectively (range: 41-464 µg/kg). The range of As in leafy vegetables from Sathkhira, Rajshahi and Comilla districts was 100-790 µg/kg (Williams et al. 2006). Arsenic level was much lower for both leafy and non-leafy vegetables in this study compared to the study of Williams et al. (2006).

The mean and median As concentration in cooked vegetables was detected as 356 µg/kg and 288 µg/kg, respectively, with a range of 98-754 µg/kg. Based on 39 cooked vegetable samples from the Munshiganj and Monohordi of Bangladesh, the mean and range of As was reported 333 µg/kg and 19 to 2334 µg/kg, respectively (Smith et al. 2006). Although the mean As concentration in cooked vegetables of this study is comparable with Smith et al. (2006) study, the maximum As was much lower.

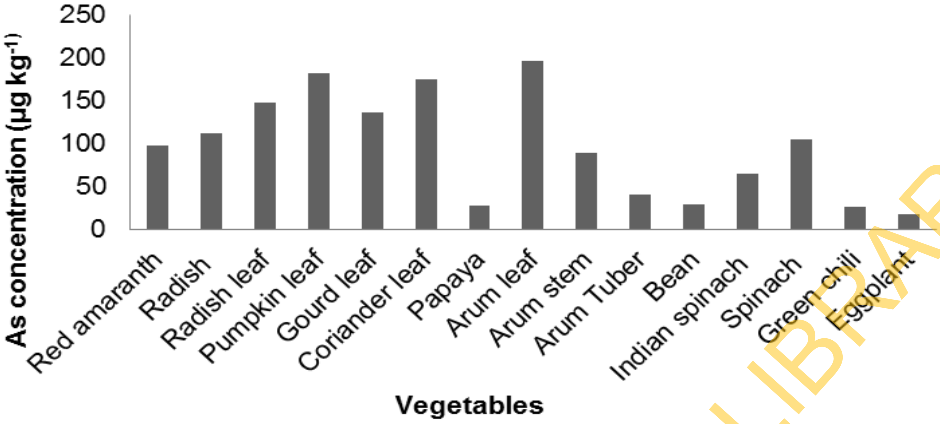

Fig. 1. Concentrations of As in home grown vegetables

An average 87% of the total As was present as inorganic form. Smith et al. (2006) reported an average of 96% inorganic As in cooked samples of Bangladesh. According to the Joint Expert Committee on Food Additives (JEFCA) recommended provisional tolerable intake of As 15 µg/kg/week. The vegetables consumption rate for adult males and females (n=71, age range 12 - 80 years) was an average 205g. Therefore, 205g vegetables could deliver a dose of between 3 - 36 µg of As daily, calculated from this study. As there is no safe limit of As so this small amount may contribute chronic exposure from consumption of home grown vegetables.

CONCLUSIONS

From the study, it is concluded that the concentrations of As varied considerably from vegetables to vegetables types. Arsenic concentration in leafy vegetables was higher than the non-leafy vegetables. None of the vegetable samples exceeded the previous recommended provisional tolerable weekly intake of As 15 µg/kg/week. As vegetable contained high percentage of inorganic As, which cause the real As related health risk to the study population.

REFERENCES

Alam, M.G.M., Snow, E.T., Tanaka, A. (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. *Sci. Total Environ*. 308:83–96.

Das, H.K., Mitra, A.K., Sengupta, P.K., Hossain, A., Islam, F., Rabbani, G.H. (2004) Arsenic concentrations in rice, vegetables, and fish in Bangladesh: a preliminary study. *Environ. Intl.* 30:383–7.

Rahman, MM, Naidu, R, Bhattacharya, P. (2009a) Arsenic contamination in groundwater in the Southeast Asia region. *Environ. Geochem. Health* 31:9–21.

Rahman, M.M., Owens, G., Naidu, R. (2009b) Arsenic levels in rice grain and assessment of daily dietary intake of arsenic from rice in arsenic-contaminated regions of Bangladesh-implication to groundwater irrigation. *Environ. Geochem. Health* 31:179-187.

Smith, N.M., Lee, R., Heitkemper, D.T., Cafferky, K.D., Haque, A., Henderson, A.K. (2006) Inorganic arsenic in cooked rice and vegetables from Bangladeshi households. *Sci. Total Environ.* 370:294–301.

Williams, P.N., Islam, M.R., Adomako, E.E., Raab, A., Hossain, S.A., Zhu, Y.G., Feldmann, J., Meharg, A.A. (2006) Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. *Environ. Sci. Technol.* 40:4903-4908.

CLEANSING A POISONED PLANET: CHEMICALS, SCIENCE COMMUNICATION AND GLOBAL PEOPLE POWER

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ABSTRACT

Earth, and all life on it, are being saturated with anthropogenic chemicals and wastes, in an event unlike anything in the previous four billion years of our planet's story. Each moment of our lives, from conception to death, we are exposed to thousands of substances, some lethal, many toxic and most of them unknown in their effects on our health or on the natural world. There is no escaping them. This has happened in barely the space of a single lifetime.

Humanity currently manufactures around 144,000 different chemicals (ECA 2015) and releases >2000 new ones a year (US DoHHS 2015), many of them untested for safety (UNEP 2013). These are the tip of the iceberg: Humanity also releases <250 gigatonnes of fossil fuels, carbon, topsoil, hazardous wastes, minerals, materials and mineral wastes. These anthropogenic substances and their impacts are now circulating throughout the Earth system – in water, air, soil, wildlife, fish, food, trade, in people and their genes. Science has detected them in the stratosphere, in cities, water supplies, from coastal fringes to the ocean depths; from the peak of Mt Everest to remote Pacific atolls and wilderness; from the Arctic to the Antarctic. (Multiple sources cited.)

Tests reveal that humans in most societies now carry a lifelong chemical burden (US CDC), that unborn babies are being contaminated with industrial chemicals (EWG 2009) and that mothers' milk in 68 countries is contaminated with pesticides and other noxious substances (UNEP/WHO 2013). WHO/UNEP (2013) estimate that one in 12 humans die from environmental poisons and around 86 million are maimed each year: this toll is greater than for HIV, malaria or car crashes. One in five cancers (<2m/yr) are attributed to environmental exposure to carcinogens.(WHO 2011) Medical scientists warn of a 'silent pandemic' of childhood brain disorders due to the global release of neurotoxins by human activity (Grandjean & Landrigan, 2014). Health officials caution that reproductive and hormonal disorders are on the rise worldwide. (WHO 2012). Above all, health researchers are concerned at the impact of mixtures of thousands of different substances combined in the human diet and living environment, which they link to conditions including developmental disorders, sexual dysfunction (including sterility), nerve and brain diseases (including autism, depression, Parkinson's and Alzheimer's), cancers and heart disease. (Carpenter et al, 2002)

Regulation has so far banned 19 out of 144,000 chemicals (Stockholm Convention, 2015) and appears powerless to stem the global flood of new releases, especially as the bulk of world chemical output is now shifting to ill-regulated Third World sites. (UNEP 2013). From Minamata to Fukushima a string of toxic disasters have demonstrated the futility of legal action against individual companies as a check to global contamination.

CONCLUSIONS

The paper explores new opportunities and public communication strategies to reduce the toxic risks arising out of overuse and misuse of unsafe chemicals globally. It proposes ways that consumers and citizens can encourage and incentivise industry to adopt green chemistry, cradle-to-cradle, clean-up and other enlightened methods and technologies. It looks at the profound changes in human thought and the market being wrought by social

media and gender equality and the likely market impact of this on anthropogenic chemical production and release. It offers ten recommendations for cleaning up the world.

It concludes by proposing a new Human Right under the Universal Declaration – a Right Not to Be Poisoned. A right enjoyed by all our ancestors prior to the modern age. It argues that without such a right there will never again be a day when humanity is not poisoned by our own emissions. (Cribb 2014)

REFERENCES

European Chemicals Agency, February 2015,
United Nations Environment Program (UNEP), Global Chemicals Outlook: Towards Sound Management of Chemicals, February 2013.
US Department of Health and Human Services, National Toxicology Program, December 2014.
US CDC, Fourth National Report on Human Exposure to Environmental Chemicals, August 2014.
Environmental Working Group (EWG), Toxic Chemicals Found in Minority Cord Blood, December 2, 2009
WHO/UNEP, Results of the global survey on concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization, Stockholm Convention Report, Geneva, May 2013.
WHO, Environmental and occupational cancers, Fact Sheet 350, March 2011.
Grandjean P and Landrigan PJ, Neurobehavioural effects of developmental toxicity, The Lancet, 14 February 2014.
WHO, State of the science of endocrine disrupting chemicals, 2012.
Carpenter DO, Arcaro K and Spink DC, ‘Understanding the human health effects of chemical mixtures’, Environmental Health Perspectives, 100, 2002, pp. 259–69
Stockholm Convention. Listing of POPs in the Stockholm Convention, 2015
Crib JHJ, Poisoned Planet, Allen & Unwin, 2014.

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HUMAN GUT MICROBIOTA — ARE THESE KEY TO EFFECTIVE FUNCTIONING OF HUMAN METABOLISM

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INTRODUCTION

It has long been recognised that the human gut harbours diverse microbes that play a fundamental role in the well-being of their host. The human body carries about 100 trillion microorganisms in its intestines, a number ten times greater than the total number of human cells in the body (Guarner and Malagelada 2003). Only a small proportion of these microbes can be cultured and as a consequence there are many colonies of microbes in the human gut that are yet to be fully studied. However recent techniques in genetic sequencing are illuminating the different microbial species and their genes in the human gut. The human gut microbiota is dominated by members of only two with more than 90% of the species belonging to Firmicutes and Bacteroidetes (Tremaroli and Bäckhed 2012). Some microbes have an intimate symbiotic relationship with the host while some could have a catastrophic parasitic relationship. It is now increasingly being recognised that individual variations in the gut microbe (microbiome) can influence host health and this may be implicated in disease etiology, and drug metabolism, toxicity, and efficacy. However, the molecular basis of these microbe–host interactions, the functional distribution of diversity and the roles of individual bacterial species are obscure. In this paper we present an overview of human gut microbiota, their role in defining human health and potential impact of contaminants on gut microflora.

COMPOSITION OF MICROBES IN GASTROINTESTINE

Variation in microbial species in the gut differs not only markedly between individuals (Yatsunenko et al. 2012), within an individual the gut microbiota is not homogenous—its density and composition varies throughout the intestinal tract. The density of bacteria in the stomach is 10^1–10^3 cells per ml of content which increases longitudinally and rises to 10^{11}–10^{12} cells per gram of colonic content in the large intestine (Fig. 1). In addition to longitudinal heterogeneity, another density gradient is found along the tissue–lumen axis (with fewer bacteria adhering to the intestinal epithelium tissue or mucus but a large number being present in the lumen). Bacterial diversity in the gut also increases along the same axis and in similar way (O'Hara and Shanahan 2006, Sekirov et al. 2010).

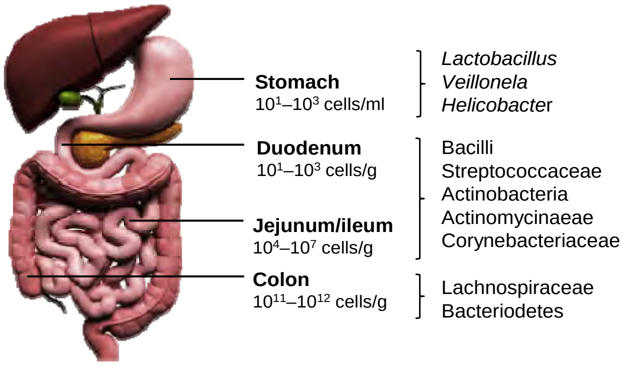

Fig. 1. Variations in microbial numbers and composition across the length of the gastrointestinal (GI) tract (O'Hara and Shanahan 2006, Sekirov et al. 2010).

ROLE OF GUT MICROBIOTA IN HUMAN HEALTH

The recognition of the role of gut microbiota in human health dates back to early human civilisation and as a consequence many societies created and consumed cultured products such as yoghurt and cheese as part of their daily dietary intake (Campbell-Platt 1994). Modern tools have now enabled microbiologists to recognise that the human gut microbiota have important and specific metabolic, trophic and protective functions. Any alteration in the composition of the gut microbiota which leads to an alteration of the normal balance can lead to an initiation of several diseases including obesity, malnutrition, inflammatory bowel disease, neurological disorders and colorectal cancer (Lozupone et al. 2012).

INTERACTIONS BETWEEN GUT MICROBIOTA AND ENVIRONMENTAL CONTAMINANTS

The food and water we consume are often contaminated with a wide range of toxic chemicals that are associated with altered physiological functions and thereby causing numerous diseases. Once ingested, the chemicals come into contact with the gut microbiota—the largest microbial community in the human body. The gut microbiota plays an important role in mediating the bioavailability and toxicity of environmental pollutants via metabolic breakdown, biotransformation and cell binding (Duda-Chodak 2012). In animal studies a 'dysbiosis' of bacterial commensal communities is observed following oral exposure to lead and cadmium (Breton et al. 2013).

CONCLUDING REMARKS AND FUTURE DIRECTIONS

The relationship between human health and the gut microbiota has become more apparent with the demonstration of the link between alteration of microbial composition and subsequent development of several physiological disorders. The effect of exogenous factors such as antibiotic administration on the gut microbial community causing 'dysbiosis' has been well documented in several reports in recent years. However, remarkably few studies have investigated the influence of environmental contaminants including heavy metals and carcinogens. The increasing trend of toxic chemicals contaminating the environment and human diet has become a serious problem in the modern world. Toxic chemicals may enter the food chain ranging from a single element to a mixture of several compounds. Therefore, more investigation of the ecotoxicology inside the gut would provide a better understanding of the interaction between toxic contaminants and the gut microbial community. Recent advances in metagenomics and bioinformatics will enable systems-level analyses of the communication between the microbiota and the hosts. Animal models can be used in toxicity studies to predict the human gut responses. Pigs have similar GI tract and diet to humans and consequently they could serve as useful animal models in gut ecotoxicity analysis.

REFERENCES

Breton, J., Daniel, C., Dewulf, J. et al. (2013) Gut microbiota limits heavy metals burden caused by chronic oral exposure. *Toxicol. Lett.* 222:132–138.

Campbell-Platt, G. (1994) Fermented foods — a world perspective. *Food Res. Int.* 27:253-257.

Duda-Chodak, A. (2012) The inhibitory effect of polyphenols on human gut microbiota. *J. Physiol. Pharmacol.* 63:497–503.

Guarner, F. and Malagelada, J-R. (2003) Gut flora in health and disease. *Lancet.* 361:512–519.

Lozupone, C.A., Stombaugh, J.I., Gordon, J.I. et al. (2012) Diversity, stability and resilience of the human gut microbiota. *Nature*. 489:220–230.

O'Hara, A.M. and Shanahan, F. (2006) The gut flora as a forgotten organ. *EMBO Rep.* 7:688–693.

Sekirov, I., Russell, S.L., Antunes, L.C. et al. (2010) Gut microbiota in health and disease. *Physiol. Rev.* 90:859–904.

Tremaroli, V. and Bäckhed, F. (2012) Functional interactions between the gut microbiota and host metabolism. *Nature.* 489:242–249.

Yatsunenko, T., Rey, F.E., Manary, M.J. et al. (2012) Human gut microbiome viewed across age and geography. *Nature*. 486:222–227.

TOTAL ARSENIC LEVELS IN RICE FROM BANGLADESH AND HUMAN HEALTH IMPLICATIONS

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ABSTRACT

Arsenic (As) bioaccumulation in rice grain has been identified as a major problem in many parts of the world. High As exposure through rice grain poses a potential significant health risk, especially people who are heavily dependent on rice based diet. In this study, we analyzed rice samples collected from Bangladesh to determine the total arsenic content in rice grain to estimate the health risks to humans. The source of variation was dominated by the location and the rice variety. Total arsenic content in rice grain ranges from between 3 - 680 µg kg^{-1} (dry weight). Rice grain samples from Faridpur, Narayanganj and Naogaon districts had total arsenic content greater than 400 µg kg^{-1} and dietary intake of arsenic from these rice grains exceeds the recommended provisional tolerable intake of arsenic 15 µg kg^{-1} week^{-1}.

INTRODUCTION

Exposure to As, a class 1 carcinogen for which there is no safe dose, affects hundreds of millions of people worldwide especially for people consuming a lot of rice in their diet. In many countries, where the concentrations of arsenic in irrigation water and soils are high, there is significant potential for human exposure via food chain issues. Rice is more efficient in bioaccumulation of arsenic than other cereal crops (Williams et al. 2007) and has led to a ten-fold elevation in rice grain concentrations in some areas and elevated in soils. Several studies have focused on As concentrations in rice grains and exposure through rice intake in worldwide. The highest level of As, up to 2.05 mg kg^{-1} (range, 0.05–2.05 mg kg^{-1}), was reported in the southern part (Gopalganj, Rajbari and Faridpur) of Bangladesh (Islam et al., 2004). Many other studies also reported high As levels in Bangladeshi rice from contaminated areas: 0.26–0.58 mg kg^{-1} (Ohno et al., 2007), 0.02–0.56 mg kg^{-1} (Rahman et al., 2009). The arsenic level of rice grains typically ranges from 3 to 680 µg kg^{-1}, and many people in Asia eat at least 200 g day^{-1} of rice. Therefore, the levels in rice commonly lead to arsenic exposures at or above the WHO's limit for water of 10 µg L^{-1}.

METHODS

Rice samples were collected from a range of geographic location household surveys throughout 74 upazilas (second administrative level of Bangladesh) of 20 districts of Bangladesh. Concentrated nitric acid (trace analysis grade) was used for the digestion of the rice samples by the procedure of Rahman et al. (2009). An Agilent 7500c (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of As in digested rice grain samples. Trace elements in rice flour (SRM 1568a) from the National Institute of Standard and Technology (NIST), USA was used to verify the analytical results for As.

RESULTS AND DISCUSSION

The mean and median As concentrations in rice grains were 126 µg kg^{-1} and 103 µg kg^{-1}, respectively, with a range of 3-680 µg kg^{-1} (dry weight). The source of variation was dominated by the locations and the rice variety. Rice grain samples from Chandpur, Dhaka, Faridpur, Munshiganj, Narayanganj and Noakhali districts had total arsenic content greater than 400 µg kg^{-1}. The study shows that on an average 81 % of total As were present as inorganic forms. Ohno et al. (2007) reported that 87-107% inorganic As present in raw rice samples of Bangladesh compared to the total As observed in nitric acid digestion.

Similar to many other Asian countries, rice is the staple food for Bangladeshi villagers. The daily estimated average As intake from some rice varieties ranged between 182 to 306 µg kg^{-1} considering the daily consumption rate for adult was an average 450 g (Table 1). Based on the intake rate and the median As concentration (131 µg kg^{-1}) the estimated daily dietary intake of As from rice was 56.4 µg kg^{-1} was reported by Rahman et al. (2009). Chowdhury et al. (2001) also reported the daily dietary intake of As from rice was 268 µg kg^{-1} from Kolsur village in West Bengal. In recent the provisional maximum tolerable daily intake of As has been withdrawn and there is no "safe" level of exposure to inorganic As so consumption of rice may cause chronic exposure of As. The results clearly indicate that the peoples are at high risk of As toxicity from rice grain.

Table 1. Rice varieties contains greater than 400 µg kg^{-1} As and estimated weekly intake through rice consumptions.

Rice Variety	tAs content (µg kg^{-1})	As intake (µg day^{-1})	WI (µg kg^{-1} body weight)	%PTWI
BINA dhan7	680	306	36	238
BRRI dhan28	515	232	27	180
BRRI dhan28	463	208	24	162
BRRI dhan29	448	202	24	157
Swarna 5	405	182	21	142
BRRI dhan49	405	182	21	142

CONCLUSION

Some of the rice samples alone contribute around 142 to 238 %PTWI of As to adults in As-prone areas of Bangladesh. Rice contained high percentage of inorganic As and ingestion of these As-contaminated rice act as a exposure route to human in any stage of life.

REFERENCES

Chowdhury, U. K., Rahman, M. M., Mandal, B., Paul, K., Lodh, D., Biswas, B. K., Basu, G. K., Chanda, C. R., Saha, K. C. & Mukherjee, S. C. 2001. Groundwater arsenic contamination and human suffering in West Bengal, India and Bangladesh. *Environ Sci,* 8**,** 393-415.

Islam, M., Jahiruddin, M. & Islam, S. 2004. Assessment of Arsenic in the Water-Soil-Plant Systems in Gangetic. *Asian Journal of Plant Sciences,* 3**,** 489-493.

Ohno, K., Yanase, T., Matsuo, Y., Kimura, T., Rahman, H.M., Magara, Y. & Matsui, Y. 2007. Arsenic intake via water and food by a population living in an arsenic-affected area of Bangladesh. *Science of The Total Environment,* 381**,** 68-76.

Rahman, M., Owens, G. & Naidu, R. 2009. Arsenic levels in rice grain and assessment of daily dietary intake of arsenic from rice in arsenic-contaminated regions of Bangladesh—implications to groundwater irrigation. *Environmental Geochemistry and Health,* 31**,** 179-187.

Williams, P., Raab, A., Feldmann, J. & Meharg, A. 2007. High levels of arsenic in South Central US rice grain: consequences for human dietary exposure. *Environ. Sci. Technol,* 41**,** 2178-2183.

HUMAN HEALTH IMPLICATIONS OF ARSENIC LEVELS IN A TROPICAL OPEN LAGOON

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INTRODUCTION

Heavy metal contamination of coastal lagoon poses a major environmental and human health concern. High levels of arsenic encountered in marine fish are predominantly in the nontoxic arsenobetaine form (De Gieter *et al.,* 2002, Baeyens *et al.,* 2009). The accumulation of heavy metals including arsenic (As) in the tissues and membranes of marine organisms depends on the exposure pathway and diet. The Lagos lagoon, a tropical estuarine ecosystem and habitat for a wide array of fisheries resources has been subjected to different anthropogenic pressures by virtue of its position. One of the main environmental concerns in this region is pollution by toxic metals which have been reported as disrupting the state of ecological equilibrium and the diversity of fisheries resources. (Don-Pedro *et al.,* 2004; Chukwu, 2006a; Ajagbe *et al.,* 2012). As long as human-induced generation of toxic trace metals persists, evaluation of the levels and the associated risk in aquatic ecosystems, particularly in species that serves as food to man is pertinent.

METHODS

Water, Sediments, Fish (*C. nigrodigitatus, M. cephalus, L. falcipinnis* and *B. soporator*) and edible gastropod (*Tympanotonus fuscatus*) were collected from the lagoon for a period of 18 months (July 2013-January 2014) during the wet and dry months. The pre-processed samples were analysed for total Arsenic levels at the Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia following standard methods and procedures.

Samples Digestion and Analysis

Filtered and acidified water samples were analyzed without digestion and Aqua regia was used for the digestion of sediments (Rahman *et al.,* 2013). Muscle tissues of biota were digested using a mixture of HNO_3 and H_2O_2. An Agilent 7500c Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Agilent Technologies, Tokyo, Japan) was used for As determination. The quality of procedure was checked using Certified Reference Materials (DORM-3 and NIST 2711l).

Health implications of arsenic levels

To estimate the human health risk from consuming fish species and edible gastropod, the Target hazard quotient (THQ) was calculated as per US EPA Region III Risk-Based Concentration Table; while the Target cancer risk (TR) was used to indicate carcinogenic risks (USEPA 2011).The equation used for estimating THQ was as follows:

THQ = (MC x IR x10-3 x EF x ED)/ (RfD x BWa x ATn)

Where, THQ is the target hazard quotient, MC is the metal concentration in fish (µg g-1); IR is the fish ingestion rate (g day-1); EF is the exposure frequency (day year-1) or number of exposure events per year of exposure, ED is the exposure duration, total for adult (year); RfD is the reference dose (µg g-1 day-1); BWa is the body weight, adult (kg) and ATn is the averaging time, noncarcinogens (day year-1).

Results and Discussion

The concentration of arsenic in water, sediment and edible soft tissues of four demersal fish and edible gastropod is presented in Table 1. The levels of accumulations varied among fish species and gastropod; may relate to their very efficient storage detoxification systems and/or due to the biological needs of the biota for arsenic (arsenobetaine).The relatively higher levels in *T. fuscatus* (4.5188 ± 138 mg/kg/dw) can also be explained by the physiology and feeding needs of the organism. Otitoloju and Don-Pedro, 2004 had earlier demonstrated that *T. fuscatus* is able to concentrate heavy metals in its soft tissues from binary mixtures of heavy metals in both field and laboratory experiment. The calculated THQs were lower than USEPA (2011) guideline value of 1 for As in fish species with the exception of *T. fuscatus* (Table 1).

Table1. Mean concentrations, target hazard quotients (THQs) and target cancer risk (TR) for intake of Arsenic for edible Biota from the Lagos Lagoon Ecosystem, Southwest-Nigeria

Sample	Mean concentration	Range	BSAF	THQ	TR
Lagoon water (n=45)	0.0012 ± 0.00 (mg/l)	0.000-0.004			
Lagoon Sediment (n=45)	2.4413 ± 0.27 (mg/kg)	0.21-7.97			
C. nigrodigitatus (n=22)	0.6686 ± 0.08 (mg/kg)	0.21-1.41	0.274	0.61	1.2 x 10^{-4}
M. cephalus (n=22)	0.7406 ± 0.12 (mg/kg)	0.25-2.27	0.303	0.68	1.3 x 10^{-4}
L. falcipinnis (n=14)	0.9843 ± 0.15 (mg/kg)	0.47-2.26	0.403	0.90	1.7 x 10^{-4}
B. soporator (n=12)	0.8558 ± 0.23 (mg/kg)	0.00-2.41	0.351	0.78	1.5 x 10^{-4}
T. fuscatus (n=24)	4.5188 ± 138 (mg/kg)	0.00-32.03	1.851	4.12	7.9 x 10^{-4}

BSAF – Bio-sediment accumulation factor; THQ – Target Hazard Quotient; TR – Target Cancer Risk

CONCLUSION

The study revealed low levels of arsenic in the Lagos lagoon and ascertained the safety of fisheries resources based on ANZFA (2011) set limits. However, with TR of 10^{-4}, relatively higher levels of As and a THQ greater than 1 in *T. fuscatus*, there is need for regular monitoring that takes into account other economically important edible fishery resources and toxic metals as well as estimate the 'tolerable intake' so as to determine safety of intake levels.

REFERENCES

Ajagbe, F. E.; Otitoloju, A. A. and Osibona, A.O (2012). Diversity of the edible fishes of the Lagos Lagoon, Nigeria and the public health concerns based on their Lead (Pb) content. *International Journal of Fisheries and Aquaculture* Vol. 2**(3),** pp. 55-62, 9.

ANZFA (2011).Australian and New Zealand Food Standards Code, Standard 1.4.1-Contaminants and Natural Toxicants (F2011C00542).

Baeyens, W., Gao, Y., De Galan, S., Bilau, M., Van Larebeke, N. & Leermakers, M. (2009). Dietary exposure to total and toxic As in Belgium: Importance of As speciation in North Sea fish. *Molecular Nutrition & Food Research*.

Chukwu, L.O. (2006a) Short-term toxicology and accumulation of heavy metals by African giant prawn, *Macrobranchium vollenhoevenii* (HERKLOTS, 1857) on exposure to treated industrial effluents. Ecology Environment and Conservation **12(1):**1-7

De Gieter, M., Leermakers, M., Van ryssen, R., Noyen, J., Goeyens, L., & Baeyens, W. (2002). Total and toxic arsenic levels in North Sea Fish. Archives of Environmental Contamination and Toxicology, **43,** 406–417.

Don-Pedro, K. N; Oyewo, E. O & Otitoloju, A. A. (2004).Trend of Heavy Metal Concentrations in Lagos Lagoon Ecosystem, Nigeria. *West African Journal of Applied*

Rahman, M.M. Asaduzzaman, M. & Naidu, R (2013). Consumption of arsenic and other elements from vegetables and drinking water from an arsenic-contaminated area of Bangladesh. *Journal of Hazardous Materials* 262, 1056–1063.

USEPA (2011). USEPA Regional Screening Level (RSL) Summary Table: November 2011. Available at http://www.epa.gov/regshwmd/risk/human/Index.htm, last update: 6th December, 2011.

A HISTORICAL DEVELOPMENT OF CHEMICAL MIXTURES HEALTH RISK ASSESSMENT METHODS AND APPLICATIONS

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INTRODUCTION

Environmental risk assessments of chemical mixtures are internationally recognized as important to understanding potential human health risks from pollutant exposures. Risk assessment methods research, statistical modelling, combination toxicology and epidemiology studies have increased knowledge since the 1980s. Although technically complex methods have been developed to assess mixtures (e.g., pharmacokinetic modelling, whole mixture approaches), simple additivity-based approaches are used on a global scale and are the focus of this presentation. Early work on mixtures risk was accomplished in the United States (US) and Europe. Importantly, legislation often drives mixtures risk research and applications. Two key US laws mandating the evaluation of mixtures are the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, which led to guidelines for assessing Superfund sites, and the Food Quality Protection Act (FQPA) of 1996, which led to evaluations of cumulative exposures to pesticides sharing a common mechanism of toxicity. In Europe, the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation motivated research on chemical mixtures risk assessment.

DESCRIPTION

In the 1980s, additivity-based methods were first applied by the American Conference of Governmental Industrial Hygienists (ACGIH, 1983) for occupational exposures, by the US Environmental Protection Agency (EPA, 1986) in Mixtures Risk Assessment Guidelines that endorsed the Hazard Index and Response Addition methods (applied to mixture components with similar and independent toxic action, respectively), and by international researchers using Toxicity Equivalence Factors (TEFs) to evaluate dioxin-like compounds (DLCs) (EPA, 1989). The EPA's 1986 Guidelines recommended a three step evaluation of mixture data that has endured over time as follows: 1) if toxicity data on the mixture of concern (MOC) are available, the risk assessment is conducted using these preferred data; 2) if toxicity data on a "sufficiently similar" mixture are available, the risk assessment for the MOC is derived from health effects data on the similar mixture; 3) if toxicity data are only available on the mixture's component chemicals, the risk assessment is conducted using a simple additivity approach.

Since the 1980s, development of component-based additivity methods (e.g., Relative Potency Factors (RPFs), TEFs) and of those used to evaluate whole mixtures has continued; EPA responded by publishing a Supplement to the 1986 Guidelines that included these methods (EPA, 2000). Also during this time, the DLC TEFs were published by the World Health Organization (WHO) to assess all health endpoints from all exposure routes/pathways, durations and dose ranges (Van den Berg et al. 2006). To generalize the TEF method, US EPA articulated the RPF approach. RPFs are computationally similar to TEFs, but apply to more situations by limiting the assessment scope, e.g., to a specific health endpoint, exposure route, and/or dose range (EPA, 2000, 2002). The US Massachusetts Department of Environmental Protection (MADEP, 2002) developed an innovative approach to assessing petroleum hydrocarbon (PH) mixtures at contaminated sites by determining analytically defined PH fractions and assigning toxicity values to those fractions. A single surrogate chemical from each fraction was used to represent risk for the entire fraction; the HI and response addition are then applied by adding across the fractions. US EPA derived additional PH toxicity values and published enhancements of this approach (EPA, 2009). To address potential toxicological interactions, a weight of evidence method was published by the Agency for Toxic Substances and Disease Registry (ATSDR, 2004) and a quantitative formula was published by EPA (EPA, 2000), for use in modifying the HI for interactions.

In Europe, the WHO held a workshop on combined exposures to chemical mixtures and published a tiered framework to aid risk assessors and managers in identifying the complexity of the needed assessment based on both exposure and hazard estimates (Meek et al. 2011). In addition, a project called NoMiracle (Novel Methods for Integrated Risk Assessment of Cumulative Stressors in Europe) has resulted in a number of projects and publications that advance understanding of chemical mixtures assessments.

The science of chemical mixtures risk assessment depends on theoretical assumptions that may be difficult to support in practice, resulting in challenges to regulatory actions. For example, dose-additive methods assume a common toxic mode of action (MOA) across the mixture components. For all of the DLCs, the MOA leading to all effects is known as aryl hydrocarbon (AH) receptor binding. In contrast, for the HI, this assumption is relaxed to only a common target organ. In reality, knowledge of MOA may be limited or too restrictive for many mixtures. The National Academy of Sciences (NAS) recommended using common adverse outcomes in the evaluation of phthalate mixtures regardless of MOA (NAS, 2008).

CONCLUSIONS

Chemical mixtures health risk assessment is a mature science whose approaches are applied to environmental contaminants internationally. However, methodological changes will be needed as new information becomes available. As toxicologists move away from animal bioassays toward computational toxicology studies and *in vitro* data, risk assessors will need to interact with these scientists, understand the data and develop new risk assessment approaches for chemical mixtures risk analysis.

REFERENCES

ACGIH. (1983) TLVS: Threshold limit values for chemical substances and physical agents in the work environment with intended changes for 1983-19084. Cincinnati, OH. p.58.

ATSDR. (2004) Guidance manual for the assessment of joint toxic action of chemical mixtures. Atlanta: ATSDR, US Department of Health and Human Services

EPA. (1986) Guidelines for health risk assessment of chemical mixtures. Federal Register 51:34014. September 24.

EPA. (1989) Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-*p*-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 update. EPA/625/3-89/016. Washington, DC.

EPA. (2000) Supplementary Guidance for Health Risk Assessment of Chemical Mixtures. ORD/NCEA. Wash, DC. EPA/630/R-00/002.

EPA (2002) Guidance on Cumulative Risk Assessment of Pesticide Chemicals That Have a Common Mechanism of Toxicity. Office of Pesticide Programs, Wash., DC.

EPA. (2009) Provisional Peer-Reviewed Toxicity Value (PPRTV) for Total petroleum hydrocarbon mixtures. 2009. Online. http://hhpprtv.ornl.gov/quickview/pprtv.php

MADEP. (2002) Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach. Final Policy. October 31, 2002. Bureau of Waste Site Cleanup, Boston, MA.

Meek et al. (2011) Risk Assessment of Combined Exposure to Multiple Chemicals: A WHO/IPCS Framework. Reg Tox and Pharm. 60:S1-S14.

NAS. (2008) Phthalates and Cumulative Risk Assessment. The National Academies Press. Washington, DC.

Van Den Berg et al. (2006) The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol Sci* 93(2):223−241.

DECISION MAKING AT CONTAMINATED SITES: ISSUES AND OPTIONS IN HUMAN HEALTH RISK ASSESSMENT

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INTRODUCTION

In the United States, state and federal regulatory agencies responsible for site cleanups develop regulations, guidance and policies that define the use of risk assessment in the decision-making process for these sites. These agencies often define default approaches, scenarios and parameters for developing risk-based screening values as a starting point for risk assessments. However, project managers and decision makers must rely on professional judgment in a risk assessment when these defaults are modified to account for site-specific conditions. While abundant resources are available to guide risk assessment, there are fewer resources to guide difficult technical decisions applying site-specific approaches, scenarios, and parameters.

APPROACH

The Interstate Technology and Regulatory Council (ITRC) is a public-private alliance that works to reduce barriers to the use of innovative environmental technologies and approaches so that compliance costs are reduced and cleanup efficacy is maximized. ITRC teams produce guidance documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision making, while protecting human health and the environment. ITRC has private and public sector members from all 50 states and the District of Columbia. From the ITRC members, a voluntary team of 60 members was assembled to discuss and identify common issues faced on projects when deviating from default approaches, formulate best practices in addressing those issues, and prepare a guidance document. Team members included representatives from state environmental agencies, community and tribal (Native American) representatives, academia, federal agencies (United States Environmental Protection Agency, Department of Defense, United States Department of Energy), consulting firms, and industry representatives. Once assembled, the team was divided into writing groups to focus on individual topics. Over a 2-year period, the team periodically met to discuss progress and content of the draft document, and incorporate internal feedback. Subsequently, draft versions of the document were sent to state and federal agencies for their review and comment, which were incorporated into the final document.

RESULTS AND DISCUSSION

The guidance document developed under this project is a resource for project managers and decision makers to help evaluate site-specific approaches, scenarios and parameters for risk assessment. Community members and other stakeholders may also find the document helpful in understanding and using risk assessment information.

This document is different than existing ITRC Risk Assessment guidance and other state and federal resources. It identifies issues commonly encountered in risk assessment related to planning, data evaluation, toxicity, exposure assessment and risk characterization, and discusses potential options to address these issues. It also addresses risk management and risk communication as they relate to risk assessment. The document includes links to resources and tools that provide even more detailed information on the specific issues and potential options.

An internet-based training course was also developed to provide an overview of this document. The training is being offered by ITRC in 2015 and 2016, with links to course registration on the ITRC website.

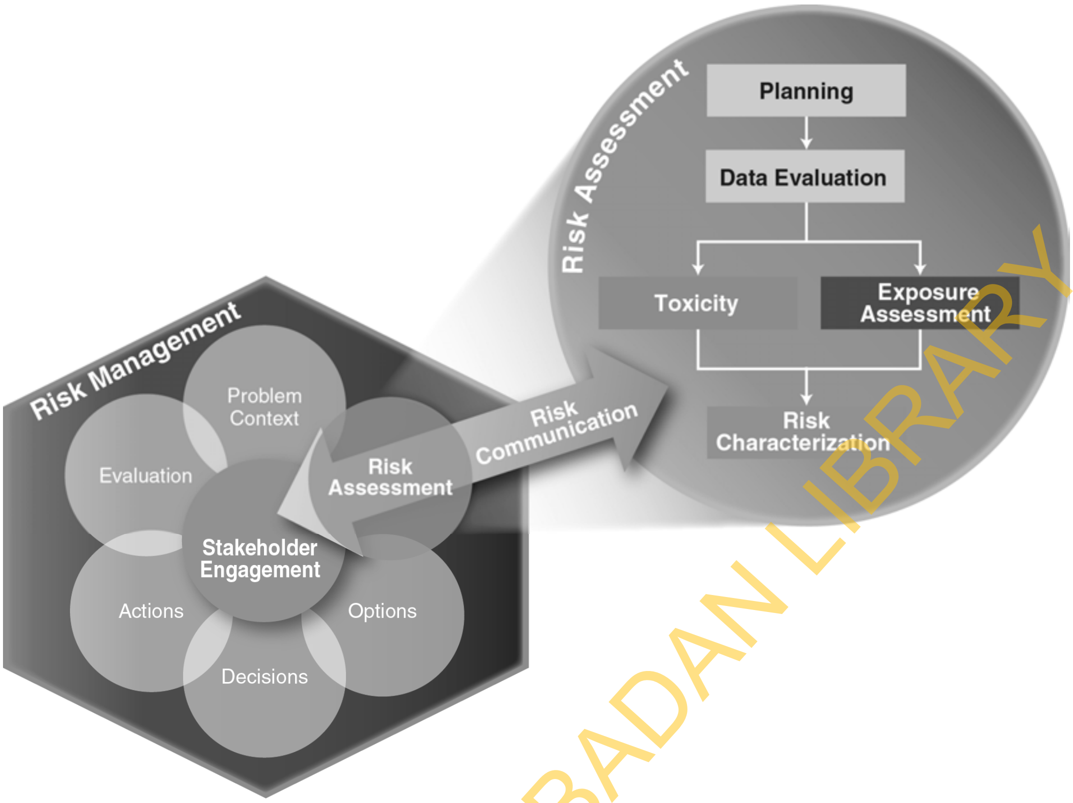

Fig. 1. Typical Framework for risk assessment.

CONCLUSIONS

The document is a useful resource for state agency project managers and other decision-makers tasked with developing or reviewing risk assessments for contaminated sites. It is also a useful tool for community members and other stakeholders who must be able to understand and use risk assessment information to make environmental decisions. The document can be used to support planning of a risk assessment, or to review the elements of a risk assessment after specific tasks have been completed.

The internet-based training that accompanies this document provides a detailed overview of the document and examples of its application.

REFERENCE

ITRC (2015) *Decision Making at Contaminated Sites: Issues and Options in Human Health Risk Assessment*. RISK-3. Washington, D.C.: Interstate Technology & Regulatory Council, Risk Assessment Team.

INNOVATIVE APPLICATIONS OF QUANTITATIVE HEALTH RISK ASSESSMENT

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INTRODUCTION

The contaminated land industry has dealt with the complexities of multi-pathway exposure to chemical contaminants using exposure modelling for many years, routinely generating assessment and clean up criteria related to site specific circumstances. However the general absence of assessment criteria representing multiple pathway exposure is a common issue in other areas too, for example in occupational hygiene, in planning new development, and in product stewardship. As a result of increasing awareness of risks associated with chemical exposures, both industry and regulators are asking for more detailed assessment of risk. This is particularly the case where complex and unpredictable mixtures of chemicals may be present. This paper presents a review of the developing scope for applications of multi-pathway quantitative risk assessment with reference to a selection of case studies from around the world.

CASE STUDIES

Mercury and Arsenic in Oil Production

Crude oil in many oilfields around the world contains sufficient concentrations of toxic metals to result in the potential for risks to workforce health and land or water contamination. Processing vessels and production platforms in affected areas encounter concentrations of metals in produced water and tank bottom sludges, including the presence of visible globules of elemental mercury. In a recent study related to onshore maintenance of equipment from production and exploration platforms, exposure via inhalation of elemental mercury vapour (well addressed by occupational exposure standards) and ingestion / dermal contact with inorganic mercury residues (not considered by occupational exposure standards) was modelled. The objective was to generate a screening value for the mercury concentration on the surface of equipment, measured using a hand held XRF, for use to determine which equipment required special handling measures. A standard exposure model was modified to use surface concentration input in mg/m^2 to estimate intake, replacing the “soil” input concentration in mg/m^3. A screening value well within the detection capability of a hand held XRF was generated; the challenge now is to provide calibration data for the several different surface materials to be tested. A similar project dealt with arsenic risks in cleaning out tank bottom sludges, again as a result of the lack of occupational hygiene criteria for direct exposure to solids and liquids, and concern over the appropriateness of control and monitoring programmes.

Health Impact Assessment for New Mining Development

A proposal for development of a new nickel mine in Indonesia resulted in a regulator requirement for a quantitative risk assessment for risks to public health via nickel exposure. Using baseline soil and groundwater data, villagers’ background exposure via food (plant uptake from crops plus literature general food intake), drinking water (groundwater) and direct contact with soil and dust (including inhalation) was modelled. Since the area was naturally nickel enriched, exposures were already close to reference toxicity values. The impacts of the proposed mine were estimated by modelling dust and chemical emissions from the mine, processing plant, and traffic movements to predict maximum airborne and deposited dust concentrations. The results showed that several villages could potentially be exposed to increased nickel, SO2, and respirable particulate concentrations as a result of mining activities. A monitoring program was recommended to provide for ongoing assessment of potential exposure during operations, together with derivation of trigger values related to background exposures for nickel. It is noted that the dust generated from the mine and traffic movements is significantly less toxic than the emissions from the nickel ore processing plant. This is primarily due to the form of nickel present, with processing emissions potentially including carcinogenic nickel subsulphide, whereas the laterite ore nickel is in complex silicate and oxide mineral structures and not readily bioavailable.

Hexavalent Chromium and Lead in Steel Surface Coatings

On discovery that a contractor had applied paint containing more than the permissible concentrations of lead and chromium to sheet steel used for roofing, the manufacturer's product stewardship department needed to determine whether a health risk to customers was possible for product already supplied. A quantitative exposure model was used to examine scenarios including roofing installation and maintenance and use of collected roof water for domestic purposes. Laboratory tests on samples of the material were used to estimate degradation, leaching and erosion of paint from the surface over time. The results indicated that even under the most pessimistic scenario, a significant health risk was not predicted. This provided the manufacturer with confidence that no harm was likely to result.

Similar assessments have been applied to workforce health risk assessment for decontamination and decommissioning of industrial building structures, including those used to contain hazardous land remediation works.

CONCLUSIONS

Multiple pathway exposure models are a flexible tool for assessment of many complex exposure problems. With relatively simple adjustments to input and output variables, pathways such as surface contact and leaching/dissolution can be added, allowing use of many kinds of analytical method to provide exposure point concentrations. Combination with fate and transport models such as atmospheric dispersion models is also very useful. The contaminated land industry has been successful in proving and demonstrating a tool that has applications well outside the industry itself, as well as in numerous associated areas such as remediation health and safety and industrial facility decontamination and decommissioning. The important features of the modelling are transparency, clear articulation of the modifications to the published model codes, and clear justification of input assumptions. Sensitivity and uncertainty analysis are also critical for multiple stakeholder acceptance of the model results. Important added value in comparison to more traditional methods includes quantification of risk and ability to determine risk-driving pathways to focus action effectively on risk reduction.

CADMIUM CHEMICAL FORM IN SOIL CONTAMINATION AND SIGNIFICANCE FOR HUMAN HEALTH RISK ASSESSMENT

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INTRODUCTION

Cadmium occurs naturally in association with zinc mineralisation but is generally present below 5000 mg Cd/kg. Normally the cadmium mineral form in zinc mineralisation is undetectable by X-ray diffraction (XRD). An approach to examine cadmium chemical form in mineralisation, mine wastes and environmental samples uses synchrotron–based X-ray absorption spectroscopy (XAS) which has sufficient sensitivity to detect environmental levels of cadmium (down to 20 mg/kg). The aim of this study was to utilise X-ray absorption near edge spectroscopy (XANES) technique to examine chemical form of cadmium in soil and mine waste of relevance to the health risk assessment process. A comprehensive approach considers cadmium chemical form in soil and its significance in health risk assessment.

METHODS

X-ray absorption spectroscopy (XANES) was used to record the cadmium K edge spectra at the Australian Synchrotron Melbourne. XANES was used to detect several cadmium chemical forms in mineral and contaminated soil samples by using linear combination fitting (LCF) of several cadmium (Cd) model compounds (Figure 1) to sample scans. Total concentrations of cadmium in aqua regia digests of soil samples were measured by ICP-MS but measured total concentrations of Cd could be better explained in terms of molecular forms. A risk assessment was conducted by using the in-vitro physiologically based extraction test (PBET) for the determination of bioaccessibility (BAc) of individual samples (Bruce et al. 2007). The BAc approach provided a practical and effective means to predict cadmium contaminant bioavailability for risk assessment of rehabilitated contaminated land.

RESULTS AND DISCUSSION

NEPC (2013) gives soil contamination guidelines for cadmium in four categories of health investigation levels (HILs) (Table 1). In the absence of site specific data, bioavailability is assumed to be 100% for risk assessment purposes. A risk assessment may incorporate the in-vitro PBET (physiologically based extraction test) determination of bioaccessibility (BAc) of individual samples (Bruce et al. 2007) to predict bioavailability of contaminated soil and to develop site-specific guideline values for remediation purposes (Table 2).
Application of XANES with LCF technique to measure % cadmium compound composition in soils gave good prediction of BAc by apportioning the relative contributions (Figure 1) to the % BAc in a sample and a more accurate explanation of BAc for risk assessment purposes. Lower % BAc of cadmium from mine wastes and house dust (Table 2) suggested the presence of low solubility cadmium sulfide while higher bioaccessibility in soil suggested the presence of more soluble cadmium carbonate, cadmium hydroxide and cadmium sulfate forms. The sum of % cadmium chemical form X RBAc gives predicted % BAc (Figure 1). The regression of measured %BAc vs. estimated %BAc from XANES LCF data gave r^2 = 0 84.

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Table 1. Soil contamination health investigation levels for cadmium (NEPC 2013)

Category of Health Investigation Levels	Cd (mg/kg)
Residential A (residential with garden/accessible soil)	20
Residential B (residential with minimal opportunities for soil access)	150
Residential C (public open space/ recreational areas)	90
Residential D (commercial/ industrial premises)	900

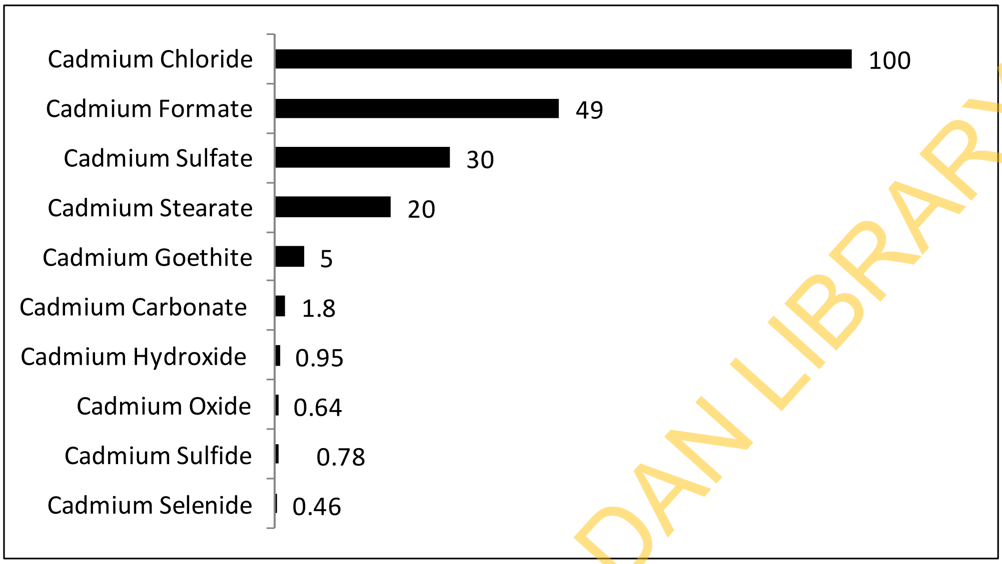

Fig. 1. **Relative bioaccessibility (RBAc) of cadmium model compounds normalised to cadmium chloride**

Table 2. Cadmium concentrations and percent bioaccessibility using PBET in mine waste, house dust and soils

	Cadmium					
	Total concentration (mg/kg)			Bioaccessibility (%BAc)		
	Mine waste (n=40)	House dust (n=4)	Soil (n=75)	Mine waste (n=40)	House dust (n=4)	Soil (n=70)
Mean	44000	30	4	20	27	36
SD	14000	14	7	20	24	17
Minimum	2.0	10	0.3	0.01	11	2
Median	360	31	2	9	17	35
95th percentile	12000	38	-	63	56	-
Maximum	78000	40	51	68	63	80

CONCLUSIONS

The present study has indicated a strong relationship between speciation and bioaccessibility and the association of cadmium with mineralised and mine processing samples when compared to surrounding soil. It is therefore important to consider zinc-mineralised samples as a source of cadmium contamination for human health risk assessment purposes.

REFERENCES

Bruce, S., Noller, B., Matanitobua, V. and Ng, J. C. (2007) *Journal of Toxicology & Environmental Health*: Part A, 70, 1700-1711.

NEPC (2013) *National Environmental Protection (Assessment of Site Contamination) Measures*, National Environment Protection Council, Adelaide.

CHALLENGES WITH SOILS CONTAMINATED BY MIXED CONTAMINANTS: BIOAVAILABILITY, BIOREMEDIATION AND ECOTOXICITY CONSIDERATIONS

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Global industrialisation coupled with modern agriculture has resulted in the production and emissions of various xenobiotic compounds into the environment. Soil, the ultimate repository/sink for most contaminants is generally encountered not with single pollutant, but with mixtures of several contaminants [organic-organic (pesticides plus their metabolites), organic-inorganic (DDT-As; PAH-metals), inorganic-inorganic (sewage sludge containing several heavy metals)]. Often the parent chemicals exist simultaneously with their degradation products. Contaminated sites are widespread and are of common occurrence in most countries, industrial countries in particular. Adverse impacts of contaminants on biological systems are primarily governed by their bioavailability which is often a major factor determining the success or failure of bioremediation. However, its success depends on several factors related to the biological agent used, soil, environmental and contaminant characteristics. Risk based remediation is currently gaining importance as an attractive option for remediation of contaminated environments. Bioavailability and toxicity are the key parameters that need to be adequately understood prior to estimating the risk posed by the contamination or any remedial activity to be undertaken. GCER and CRC CARE are therefore conducting research to examine the factors affecting bioavailability of contaminants in relation to ecotoxicity and bioremediation. A few case studies from our research on the toxicity of mixed contaminants (eg. DDT and its metabolites, petroleum hydrocarbons, Copper, cadmium - atrazine, arsenic-DDT etc) in long-term contaminated sites and the associated challenges to remediation will be discussed.

ASSESSMENT OF GROUNDWATER – SURFACE WATER INTERACTION IN A FRACTURED BASALT AQUIFER SYSTEM TO SUPPORT ECOLOGICAL RISK ASSESSMENT

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INTRODUCTION

Creeks and rivers in the western suburbs of Melbourne have developed along the margins of thick and regionally extensive basaltic lava flows. These lavas form a complex fractured aquifer system with creeks and rivers variably acting as groundwater discharge and recharge zones.

A manufacturing facility located in an area adjacent to one of these creeks was subject to an extensive ecological and hydrogeological assessment. The assessment was initiated following the identification of a contaminant plume in the basalt aquifer migrating in the direction of the creek. The contaminants mainly included nitrogen species, perchlorate and lower concentrations of chlorinated solvents (i.e. marginally above trigger levels). The objective of this assessment was to characterize the risk posed by the discharge of contaminated groundwater to the creek ecosystem.

HYDROGEOLOGICAL SETTING

The creek has developed along the margin of a younger lava flow (Fig 1). The more weathered rock of the older lava flow acted as the path of least resistance for the old surface water course to erode a new valley following emplacement of the lava.

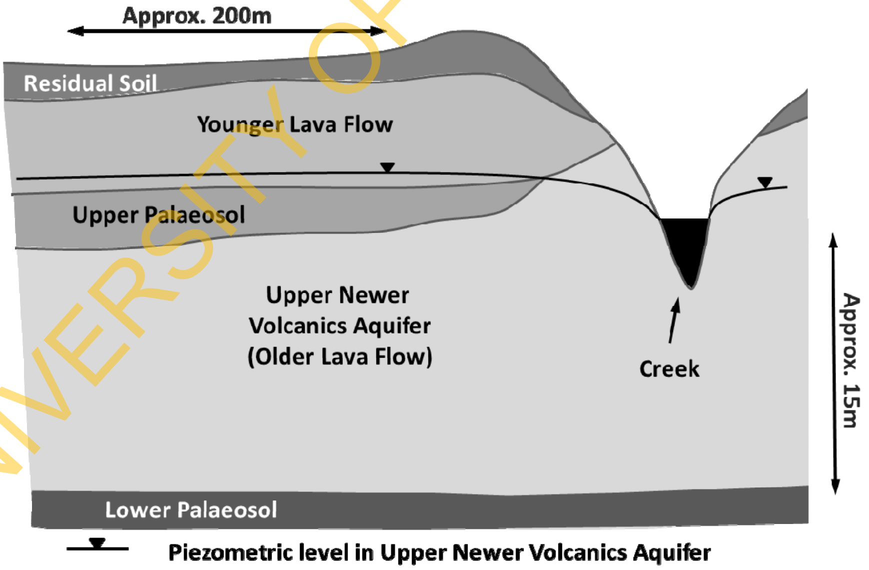

Fig. 1. Hydrogeological Setting

The new valley eroded deeper into the underlying older lava flow. The depth of the valley resulted in the older lava flow to act as the main aquifer unit of relevance with regard to the relationship between groundwater and the creek.

The older lava flow is an aquifer of regional significance, referred to as the Upper Newer Volcanics aquifer. The top and base of the aquifer are typically marked by palaeosols.

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[*] The authors want to acknowledge GHD Pty Ltd for the collection of ecological data used in this study.

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GROUNDWATER – SURFACE WATER INTERACTION

The course of the creek is characterized by a succession of riffles (areas of shallower water) and pools (area of deeper water), each of which were subject to regular monitoring (Fig 2).

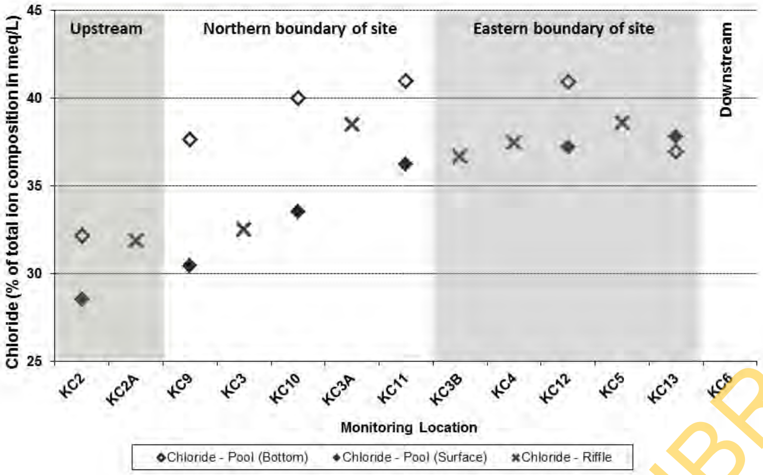

Fig. 2. Increase in Chloride as Indicator of Groundwater Contribution to Surface Water

The distribution in water levels (groundwater and surface water) and chemical indicators including electrical conductivity, total dissolved solids and major ions were used to define the creek – groundwater interaction zones (Fig. 2). The creek was indicated to act as a groundwater discharge zone from upstream of pool KC9 to downstream of pool KC12, with the discharge predominantly occurring via the pools. Further downstream of pool KC12, the creek was indicated to transition into a losing creek (acting as a groundwater recharge zone). The chemical indicators supported that pool KC12 acted as the main pathway for contaminated groundwater discharge into surface water. A diamond core drilling and nested well installation program focused on the KC12 area enabled the definition of localised flow zones within the vertical aquifer profile. The characteristics of the upper zones supported that these were connected to the creek, contributing to the contaminated groundwater discharge while groundwater within the deeper zones were indicated to underpass the creek. This was supported by the distribution of contaminants within the vertical profile.

ECOLOGICAL RISK ASSESSMENT

The understanding of the groundwater – surface water interaction provided focus to the ecological risk assessment (ERA). Effect measurements in the creek were collected to assess potential impact to receptor groups of interest from the contaminated groundwater discharge, with a particular focus on pool KC12. These included water and sediment quality data from the creek, chlorophyll a measurements in creek water as well as a range of other fauna and flora surveys (e.g. frog survey).

Of the lines of evidence collected in the ERA, there was an identified risk of growth of nuisance algae from nitrogen impacted groundwater discharge. However, growth of algae in summer is common in urban creeks around Melbourne and is a short-term problem with the algae being washed away when heavy rain occurs. The ERA concluded that growth of nuisance algae was considered to present primarily an aesthetic issue rather than adverse to the overall creek ecosystem.

The effect measurements supported the conclusion that whilst receptors in the creek were exposed to contaminants from the site via groundwater, there was no evidence of significant adverse effects.

CONCLUSION

Understanding the creek – groundwater interaction zones in combination with key vertical flow zones within the aquifer are critical to ensure that the locations used to measure ecological effects are focussed and representative for the ERA process.

LINES OF EVIDENCE USED IN ECOLOGICAL RISK ASSESSMENT OF CONTAMINATED GROUNDWATER

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INTRODUCTION

Initial assessment of groundwater and surface water at a former municipal landfill site adjacent to a river indicated metals and nutrients were above applicable guidelines. The available groundwater level and chemistry data suggested that the site groundwater was likely to be hydraulically connected to the river. These findings triggered the need for further investigation and an ecological risk assessment (ERA).

An ERA was initiated which used multiple lines of evidence in a weight of evidence approach. The source-pathway-receptor linkages were identified by development of a conceptual side model which indicated the ecological receptors potentially at threat were the saltmarsh communities located on the near-shore environment, and aquatic receptors in the adjacent estuarine river. The potential for unacceptable risk to the saltmarsh communities and river was assessed by obtaining additional field data.

Additional data included chemical (surface water, sediment, groundwater (pore-water)) and ecological data to:

- Assess if impacts were occurring to saltmarsh communities from leachate-impacted groundwater discharging from the site.
- Evaluate whether attenuation of chemicals may be occurring within the saltmarsh.

METHODS

A key component of the field program was the assessment of ecological and chemical conditions at 'impact' locations down-gradient of the site and at reference locations. Abiotic data gathered included surface water, sediment, and groundwater (pore-water). Biotic data gathered included saltmarsh vegetation community composition and abundance. These data were collected from multiple 'impact' and reference locations to test for differences among the (potentially) impacted and reference locations, and to evaluate if these differences could be attributed to contaminated groundwater from the site. The survey included more than one reference site. The inclusion of more than one reference site has been proven to increase the certainty of results and decrease the likelihood of false positives.

The data were analysed as follows:

- Abiotic data (surface water, sediment, and sediment pore-water) were compared to the ANZECC/ARMCANZ (2000) guideline values for marine ecosystems. This was to establish an understanding of:
    - Background conditions, including exceedances that may be occurring in reference locations.
    - Exceedances occurring at the potential impact locations.
- Biotic and abiotic data were analysed using PRIMER (Plymouth Routines in Multivariate Ecological Research, version 6) statistical software to assess for significant differences between reference and impact locations and whether patterns were apparent between locations or between zones (upper shore, lower shore, and river) on the shore.

- Biotic and abiotic data were also assessed by multidimensional scaling (MDS) ordination using bubble plots.

RESULTS AND DISCUSSION

Review of the data gathered to support the ERA identified:

- Chemicals of interest (or 'indicator' chemicals) reported in groundwater above guideline levels at the site included metals (boron, arsenic, and cobalt), nutrients (nitrogen) and total petroleum hydrocarbons (TPH).
- Cobalt and TPH results were below guideline or laboratory limits of reporting (LOR) in surface water and sediment at locations down-gradient of the site.
- Arsenic, boron and nitrate were reported above guidelines in pore-water at some of the down-gradient locations. The frequency of occurrence and magnitude of concentrations were noted to decrease with increasing distance from the site. Boron concentrations reported at the reference sites were the same order of magnitude as the impact sites. Boron is naturally present in seawater.
- The saltmarsh vegetation community composition at the site was not significantly different to that at reference locations.

Consequently, boron, cobalt and TPH were eliminated from the ERA. Arsenic and nutrients were considered further.

CONCLUSIONS

The potential for impact from groundwater to receiving environments was considered to be over a small spatial scale. The ERA concluded that while receptors in the river may be exposed to arsenic and nitrogen from the site via groundwater discharge, the potential for adverse effects from exposure in the receiving environment were likely to be low.

The use of data from multiple media (surface water, sediment and groundwater (pore-water) quality) at the site and at reference locations made it possible to assess whether the down-gradient concentrations were the result of contaminated groundwater from the site or related to background conditions. The assessment of impact zones (upper shore, lower shore and river) and use of PRIMER and MDS bubble plots enabled trends and variation in the data to be easily identified and interpreted. The use of biotic data confirmed the types of receptors of interest in the saltmarsh and demonstrated no impact to the community composition and abundance relative to reference sites.

REFERENCES

ANZECC/ARMCANZ (2000). Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. An Introduction to the Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

Clarke, K.R. and Warwick, R.M., 2001. Changes in Marine Communities. An approach to statistical analysis and interpretation. Second Edition. Primer E: Plymouth

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ASSESSMENT OF WEATHERED HYDROCARBON RESIDUAL TOXICITY USING ENDEMIC AUSTRALIAN FLORA AND FAUNA

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INTRODUCTION

Background

At present, Australian soil regulatory guideline values of TPH have been derived from the Canadian guidelines. This is conducive for regulatory guidelines purposes, but it is questionable whether or not these guideline values are applicable to the Australian environment. Using native Australian plant may be more realistic as an assessment tool.

Aims

- To screen Australian native grasses for their suitability as an assessment tool for weathered hydrocarbons residual toxicity.
- The initial study investigated the germination of 15 Australian grasses compared to the germination result of wheat.

METHODS

- One layer of no. 1 Whatman filter paper, one layer of glass beads and 10 mL Milli-Q water was added to 90-mm gamma-sterilized Petri dishes.
- Thirty seeds were added without pre-treatment in triplicate to each dish, sealed with parafilm, and placed in the dark at fluctuating air temperatures during the course of the day.
- Germination was assessed regularly for 20 days. Once radicals emerged, the germinated seeds were removed and counted.

RESULTS AND DISCUSSION

For germination different native Australian grass seeds require different environmental conditions, for example, light or dark, alternating temperatures (Lamb et al. 2010). Nine out of fifteen species showed different percentage of germination. A common problem for native grass is 'synchronicity'. Therefore, it is difficult to get all seeds to germinate rapidly and at the same time whilst the seed may be healthy and potentially germinable. (Groves, Hagon & Ramakrishnan 1982)

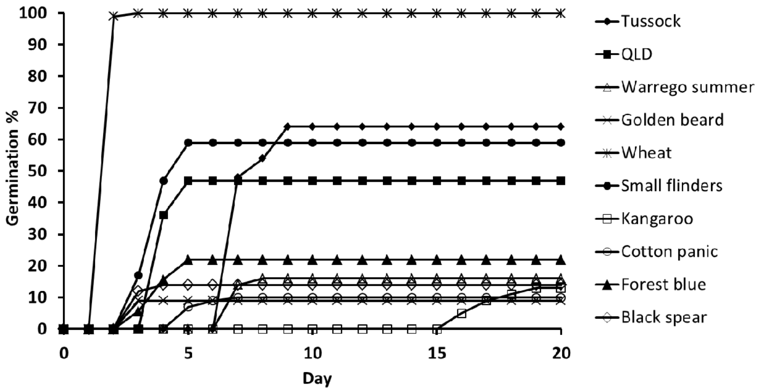

Fig 1. Germination percentage of different Native grasses and wheat

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Table 1: Experimental conditions and percentage of germination in germination trial

Common name	Scientific name	Seeds per petri dish	Optimal temperature regime (12 h/12 h)	Germination (%)	Time (day)
Tussock	*Poa labillardierei*	30	25/25	65	9
Small flinders	*Iseilema membranaceum*	30	37/37	59	5
Queensland blue	*Dichanthium sericeum*	30	25/25	47	5
Black spear	*Heteropogon contortus*	30	25/37	14	4
Warrego summer	*Paspalidium jubiflorum*	30	25/37	14	7
Kangaroo	*Themeda triandra*	30	25/18	12	20
Forest blue	*Bothriochloa bladhii*	30	25/37	10	5
Cotton panic	*Digitaria brownii*	30	25/37	9	7
Golden beard	*Chrysopogon fallax*	30	37/37	9	4
Wheat	*Triticum aestivum*	30	25/25	100	3

CONCLUSIONS

Comparing with the germination percentage of wheat, four native grass species- Tussock, Small flinders, Queensland blue and Black spear are selected for toxicity studies. Time required for germination is also a key parameter for selection.

REFERENCES

Groves, R, Hagon, M & Ramakrishnan, P 1982, 'Dormancy and germination of seed of eight populations of Themeda australis', *Australian Journal of Botany,* vol. 30, no. 4, pp. 373-386.

Lamb, DT, Ming, H, Megharaj, M & Naidu, R 2010, 'Relative tolerance of a range of Australian native plant species and lettuce to copper, zinc, cadmium, and lead', *Archives of environmental contamination and toxicology,* vol. 59, no. 3, pp. 424-432.

USING IN SITU REMEDIATION (ISR-MT3DMS) MODEL TO ESTIMATE BACK-DIFFUSION TIMEFRAME FOR THIN SILTS AND CLAYS

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INTRODUCTION

Low-permeability soils like silts and clays may act as storage reservoirs for dissolved contaminant mass. As the original source is depleted, back-diffusion may sustain groundwater plumes for decades to centuries or longer. There are some tools available for evaluating back-diffusion from thick clay/silt layers (e.g. Matrix Diffusion ToolKit); however, there are significant limitations for estimating timeframes for back-diffusion from thin layers of clay and silt, and for evaluating the influence of contaminant degradation on back-diffusion timeframe. Use of numerical models may be prohibitive in some cases, particularly for three-dimensional (3-D) models. For example, representing one thin silt or clay unit in a numerical model may require incorporation of dozens to a hundred or more model layers. Representing multiple thin silt/clay units distributed vertically is even more prohibitive.

This study presents an innovative approach for simulating diffusion using a local domain approach, which has been incorporated into a new public domain model called In Situ Remediation MT3DMS (ISR-MT3DMS). ISR-MT3DMS was developed based on the MT3DMS framework, and utilizes an array of one-dimensional local domain models for simulating diffusion-dominated processes at different spatial and temporal resolution than the global domain. ISR-MT3DMS also includes the flexible biogeochemical reaction framework from BioRedox (Carey et al., 1998) for simulating natural and enhanced degradation.

MODELING APPROACH

ISR-MT3DMS is applied to simulate back-diffusion, and the corresponding inhibition of plume strength reduction, observed at a Florida site (Parker et al., 2008) where source zone containment was implemented in an aquifer with a thin, continuous clay layer. First, the use of the local domain approach for simulating back-diffusion with ISR-MT3DMS is verified by comparison to a two-dimensional MT3DMS model. A trichloroethene (TCE) NAPL pool with length of 5 m, overlying a continuous clay layer with thickness of 0.2 m, was simulated to be present for a period of 35 years, upon which the model assumed the NAPL source was completed removed. The model then simulated back-diffusion from both the top and bottom surfaces of the thin clay layer for a period of 50 years. Grid spacing and input parameters are similar to those presented in a model originally used by Parker et al. (2008). Finally, the ISR-MT3DMS model was used to evaluate the sensitivity of back-diffusion remediation timeframe to various site characteristics.

RESULTS AND DISCUSSION

The ISR-MT3DMS model, which initially employed local domains having the same horizontal spacing as the global model (0.5 m), was verified by comparison to an MT3DMS model with the same grid spacing and input parameters. Adjusting the local domain spacing to 5 m (Figure 1) had little influence on the simulated remediation timeframe for back-diffusion. The base case model results indicate that 15 to 40% of mass discharged from the NAPL pool entered the top of the underlying clay layer. Thirty years after removal of the NAPL source, 99.96% of TCE mass had been removed from the dissolved plume (Figure 2), and yet downgradient concentrations at wells still ranged from 12 to 126 ug/L depending on screen length. A sensitivity analysis indicate that back-diffusion remediation timeframe is most sensitive to the thickness of the silt/clay unit, groundwater velocity, and total organic carbon concentration (i.e. retardation). Timeframes are moderately sensitive to transverse vertical dispersivity, length of the clay unit, and well screen length. Timeframes are least sensitive to the tortuosity coefficient, and NAPL contact time with the silt/clay unit.

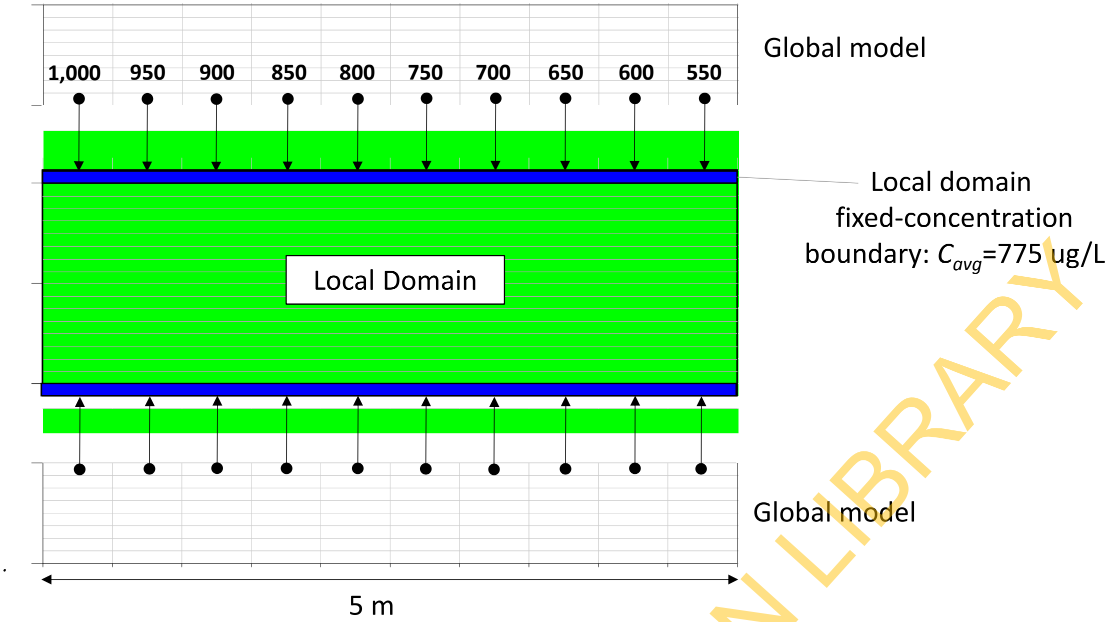

Fig. 1. Example calculation of boundary concentration in a local 1-D domain.

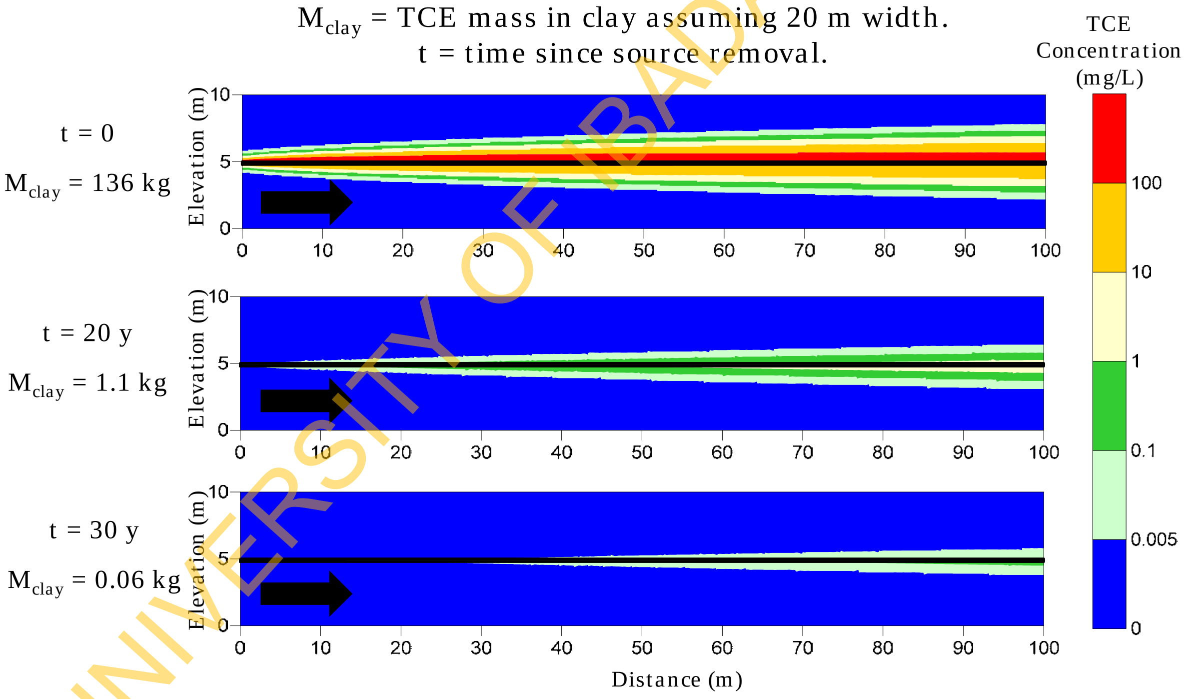

Fig. 2. Simulated TCE profiles at times of 0, 20, and 30 years after source removal.

REFERENCES

Carey, G.R., Van Geel, P.J., Murphy, J.R. (1998) BioRedox – A coupled biodegradation-redox model for simulating natural and enhanced bioremediation of organic pollutants: Version 1.0 User's Guide. Conestoga-Rovers & Associates, Ottawa, Ontario.

Carey, G.R., McBean, E.A., Feenstra, S. (2015) Estimating tortuosity coefficient based on hydraulic conductivity. Submitted to Ground Water.

Parker, B.L., Chapman, S.W., Guilbeault, M.A. (2008) Plume persistence caused by back-diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation.

FORMER CLANDESTINE DRUG LABORATORIES — HOW CONTAMINATED ARE THEY?

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INTRODUCTION

The manufacture of illicit amphetamine-type stimulant (ATS) drugs in clandestine drug laboratories is undertaken in a range of locations that include residential homes/apartments, hotels/motels, backyard sheds, commercial/industrial premises and cars. Unlike controlled manufacturing of chemicals/drugs, the manufacture of illegal ATSs results in uncontrolled storage and use of precursor chemicals, uncontrolled release of by-products including gases/aerosols, disposition of drug residues on all surfaces in the premises and uncontrolled dumping of waste materials. This can result in significant exposure and risk issues within the premises during and after the drugs have been “cooked”. These hazards and risks are typically known and managed by law enforcement (and forensic scientists), however they are not known by the general public who may subsequently live or work in the premises.

This paper aims to present the results of research into the characterisation of contamination inside residential homes in Australia, and the importance of identifying and remediating these premises prior to occupancy.

METHODS

Research is being undertaken to evaluate the range of factors that affect the level of contamination that may be present in a residential home following the manufacture of ATS, in particular methamphetamine. In addition contamination data has been collected in a range of these premises. This data has been compiled and reviewed to provide a better understanding of the level and spread of contamination in these premises.

More specifically a case study that highlights the importance of the assessment and remediation of contamination in former clandestine drug laboratories will be presented. This case study links contamination levels with health effects and highlights the risks to public health in situations where residential premises are not remediated.

RESULTS AND DISCUSSION

Contamination

Indoor surface contamination data has been obtained from New South Wales, Victoria, Queensland, South Australia and Western Australia from 99 premises where methamphetamine has been manufactured via a range of methods. These data indicate the presence of contamination in many premises that exceed the current health based guideline of 0.5 $\mu g/100cm^2$ (for residential homes) (ACC 2011) as summarised in Figure 1. The data also indicates that, in many of the premises, contamination has spread throughout the premises (not just being confined to the area of the methamphetamine cook). These data illustrate the importance of identifying, assessing and remediating former clandestine drug laboratories.

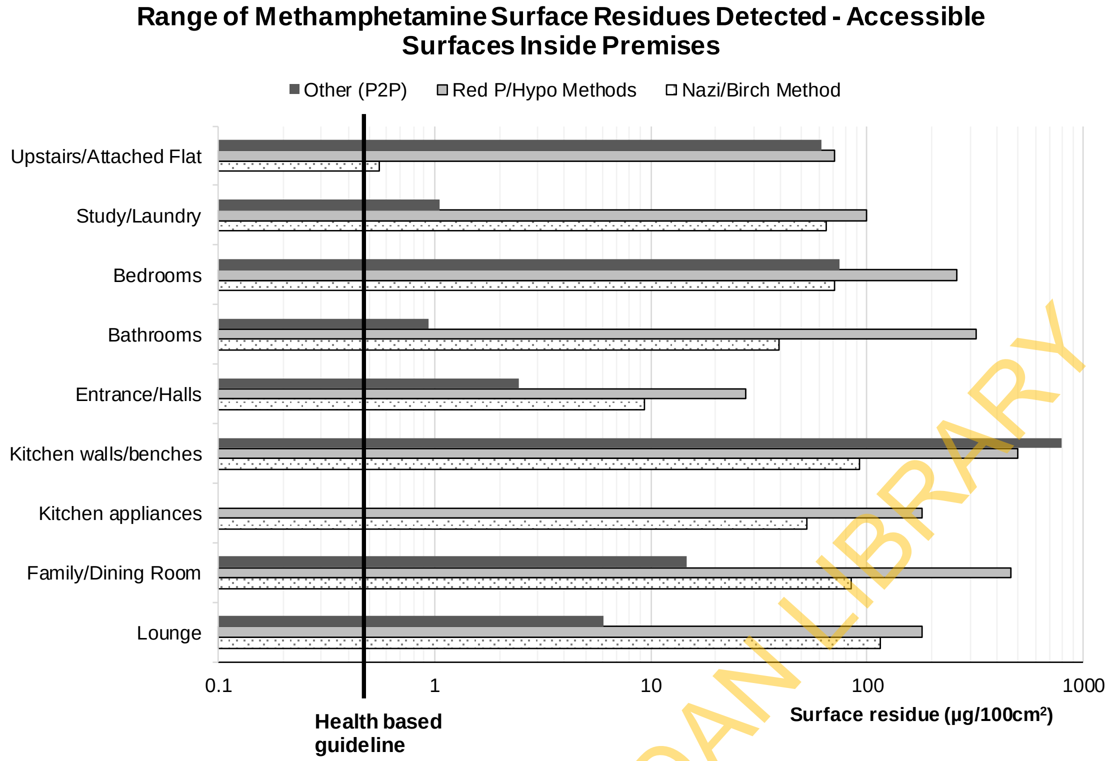

Fig. 1. Summary of surface residues reported on accessible areas in former clandestine drug laboratories in Australia (note the health based criteria is 0.5 µg/100cm^2)

Case Study

An opportunistic case study provides insight into the issues associated with a breakdown in the existing system for the identification, management and remediation of former clandestine drug laboratories and the impact of these issues on public health.

In this case study a family (2 adults and 3 children) purchased a rural property in Victoria and moved in. Approximately 8 months after moving in the local council contacted them to inform them the property had been used to manufacture methamphetamine. Subsequent testing identified methamphetamine levels in the home that were at least 50 times higher than the health based guideline. The family was relocated after living in the home for 18 months, during which time the youngest child (aged 8 years) had developed respiratory problems and noticeable behavioural changes.

REFERENCES

ACC 2011, *Clandestine Drug Laboratory Remediation Guidelines*, Commonwealth of Australia.

WHEN CONCEPTUAL SITE MODELS ARE WRONG — A CASE STUDY

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INTRODUCTION

Development of a Conceptual Site Model (CSM) is an inherent part of contaminated site assessment and management. The iterative nature of CSM development is crucial to provide guidance at even early stages of investigations and to reflect changes in understanding.

As a case study this abstract presents a summary of contaminated sites assessment undertaken for a confidential client where an error was identified in the CSM. Based on available geological information, the CSM included a potable beneficial use of groundwater which became one of the main drivers for assessment. During the assessment process, the potable resource aquifer which this beneficial use was associated with was confirmed to be absent requiring redefinition of assessment objectives and redesign of intrusive investigations.

METHODS

Site assessment commenced with a Preliminary Site Investigation (PSI) and progressed through two stages of Detailed Site Investigation (DSI). The main focus of the DSI was to assess groundwater impacts caused by leakage of tailings dams which were identified to have migrated offsite.

The available geological maps (GSWA, 1970; GSWA, 2000) indicated that the surficial formation at the site was underlain by the Yarragadee Formation, the Cadda Formation and then the Cattamarra Coal Measures. The beneficial uses for these formations were identified in the CSM as follows:

(a) Surficial Formation – beneficial use: irrigation and agricultural use
(b) Yarragadee Formation – beneficial use: potable resource aquifer
(c) Cadda Formation – hypersaline therefore no beneficial use identified
(d) Cattamarra Coal Measures – hypersaline and therefore no beneficial use identified

The potential presence of a palaeochannel was also identified in the CSM.

The Stage 1 DSI included a geophysical survey (to map the extent of the inorganic contaminants in groundwater) with the objective of providing sufficient information to enable design of the Stage 2 DSI to target the area of groundwater impacts. One of the main objectives of the Stage 2 DSI was anticipated to be to assess the impacts on the potable resource aquifer.

RESULTS AND DISCUSSION

The presence of clay underlying the survey area masked the expected resistivity signal of the inorganic contaminants and therefore the geophysical survey was unable to define the extent. However, the survey did provide valuable information on the geology underlying the survey area including the potential location of the palaeochannel and the nature of the deeper formations underlying the site. Very low resistivity material was identified at depth which, based on the geophysical contractor’s experience, was interpreted as saline water in clay. This was potentially consistent with the presence of the hypersaline Cadda Formation and Cattamarra Coal Measures but not with the expected presence of the Yarragadee Formation.

After the completion of the Stage 1 DSI, additional information was obtained that suggested the geology underlying the site may differ from the geology inferred from the geological maps. Several deep wells were installed by the Water Authority of Western Australia (GSWA, 1994, Appendix A) in the area in 1994. Borehole logs for these wells identified the deeper formation as the Cattamarra Coal Measures or the Cadda Formation at the majority of well locations. The Yarragadee Formation was only identified in one well located to the north and five wells located to the south of the site. The absence of the Yarragadee Formation would remove the beneficial use associated with this potable resource aquifer identified in the CSM.

Based on the revised CSM, the objectives for investigation were redefined:

(a) Confirm the deeper formation underlying the site i.e. Yarragadee Formation or Cadda Formation/Cattamarra Coal Measures
(b) Lateral delineation of the extent of the inorganic contaminants in groundwater
(c) Confirmation of the presence and hydraulic properties of the palaeochannel
(d) Contaminant fate and transport modelling to assess migration of inorganic contaminants in groundwater onto adjacent properties and toward sensitive environmental receptors

The Stage 2 DSI was redesigned to address these objectives and included drilling of two boreholes into the deeper formation and completion as groundwater monitoring wells. Information collection during drilling to enable identification of the deeper formation included: detailed logging, soil sampling, particle size distribution analysis, palaeontological analysis, groundwater sampling and analysis for water quality parameters (for piper plot analysis) and key contaminants of concern, hydrogeological testing, and gamma logging of completed groundwater monitoring wells.

CONCLUSIONS

The results of the Stage 2 DSI confirmed that the deeper formation underlying the site was the Cadda Formation i.e. the Yarragadee was not present. Identification of this potential error in the CSM early in the assessment process allowed the Stage 2 DSI to focus on the superficial aquifer thereby reducing costs associated with site assessment and enabling appropriate management of the risks.

The other objectives for investigation were also met: the location of the paleochannel was confirmed, lateral delineation of the inorganic contaminants in groundwater on adjacent properties was achieved, and risk assessment incorporating results of contaminant fate and transport modelling concluded low risk to downgradient sensitive environmental receptors.

REFERENCES

Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC &ARMCANZ, 2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Geological Survey of Western Australia (GSWA, 1970). Geraldton Sheet SH 50/1 1:250,000 Geological Series – Explanatory Notes.

Geological Survey of Western Australia (GSWA, 1994). Greenough Shallow Drilling Project Bore Completion Reports. Report by Hazli A. Koomberi. Hydrogeology Report No. 1994/56.

Geological Survey of Western Australia (GSWA, 2000). Geraldton Sheet 1840-II 1:50,000 Regolith – Landform Resources Series. First Edition 2000.

ASSESSING BACKGROUND CONCENTARTIONS OF INORGANIC CONTAMINANTS IN THE BRIGHTON GROUP AQUIFER, SOUTHEAST MELBOURNE

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INTRODUCTION

Determining background concentrations of chemical constituents in soils and groundwater is a critical issue for the land contamination industry, yet there is no consensus on the method of determining or defining background concentrations. The 'natural background' concentration refers to the levels that reflect natural processes uninfluenced by human activities, however it has been suggested that such a background value effectively no longer exists, considering the widespread anthropogenic influences on earth's systems (Nakic, et al., 2007). Therefore, an alternative and more practical definition that is of greater relevance to the contaminated land management industry is the 'ambient background' concentrations, considered to be levels reflecting the combination of natural and diffuse inputs of elements, in the absence of any point-source contamination (Reimann & Garrett, 2005).

In this study, the Australian Contaminanted Land Consultant's Association (ACLCA) commissioned RMIT to conduct a study into background levels of inorganic constituents in groundwater in the Brighton Group, a major aquifer in the metropolitan area of Melbourne, Australia, using statistical analysis of large datasets. Data was compiled from contaminated site investigation audit reports, along with results from a groundwater sampling campaign utilising government monitoring bores and private water supply wells. Simple statistical techniques (boxplots, frequency histograms and cumulative probability graphs) were used to analyse the data and propose a range of concentrations deemed representative of the 'ambient background' for 10 elements. This is considered to be groundwater unaffected by point source contamination, but subject to diffuse anthropogenic inputs.

METHOD

Data was acquired via two methods; firstly, through reviewing and compiling data all groundwater data reported from a total of 63 Victorian EPA Environmental Audit Report sites covering the study area and secondly, collecting groundwater samples from both government monitoring bores and private water supply wells in the aquifer (n = 21). Audit reports from sites that were heavily contaminated were excluded as data was considered to be biased and not representative of natural conditions.

The first step in determining an appropriate range for the background levels was undertaking descriptive statistics analysis and box/whisker plots. The second step involved developing frequency histograms, with the compiled concentration data for each element plotted with samples grouped by range of reported concentraitons (bins). The bin range was modified using a qualitative assessment of the number of total values falling into each concentration range. The point on the frequency histogram where the number of samples in a bin was < 1% lower than the adjacent bin was used to determine the proposed background range. For some elements (e.g. arsenic and chromium) this produced relatively clear cut-off points on the frequency histograms and the concentration range (bin) was taken as the background level. Other elements (e.g. fluoride) were more scattered and clear cut-offs more difficult to determine. This probably relates to a combination of: greater variety of sources; complexity of geochemical controls; inadequate sample size; and/or variability in detection limits and reporting ranges over the timespan of the data.

RESULTS AND DISCUSSION

An example of two frequency histograms used to determine background concentrations for arsenic and chromium is detailed in Figure 1. Table 1 presents the proposed background ranges for inorganic constituents within the study area. It is noted that results for cadmium, fluoride, mercury and nickel were inconclusive.

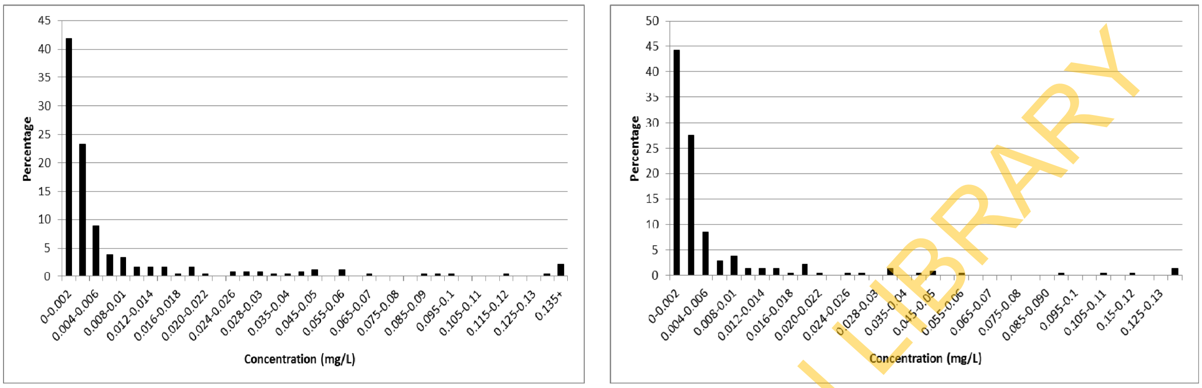

Fig. 1. Arsenic (left) and chromium (right) frequency histograms

Table 1. Proposed background levels in the Brighton Group

Constituent	Arsenic	Chromium	Copper	Lead	Nitrate	Zinc
Proposed background level (mg/L)	0.010-0.012	0.010-0.012	0.012-0.013	0.0025-0.0030	0.30-0.35	0.070-0.075

CONCLUSIONS

The background levels for a number of inorganic constituents in the groundwater in the Brighton Group are proposed. The method is based on collating and evaluating a large dataset which was compiled from contaminated site investigation audit reports and a groundwater sampling campaign. Analysis of data through frequency histograms enabled the estimation of background levels for six analytes (refer to Table 1). The approach here could be widely applied to estimate ranges of naturally occurring concentrations of inorganic constituents, provided the geochemical processes of the aquifer setting from which data is drawn are well constrained. The background levels proposed could be utilised by the land contamination industry to distinguish between the concentrations of species that is naturally occurring and contamination. These background levels have been determined on a specific study area; therefore care must be taken when applying these values to a smaller area or when extrapolating these values to areas outside the study area.

ACKNOWLEDGEMENT

This project was funded by ACLCA Victoria.

REFERENCES

Nakic, Z., Posavec, K., Bacani, A. (2007) A visual basic spreadsheet marcro for geochemical background analysis. *Ground Water* 45(5): 642-647

Reimann, C., Garrett, R.G. (2005) Geochemical background – concept and reality. *Science of the total Environment* 350: 12-27.

PERFORMANCE TESTING OF SUPER OXYGENATED WATER GENERATION AND DELIVERY METHODS

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INTRODUCTION

Super oxygenated water (SOW) is an effective technology for remediation of hydrocarbon contaminants in groundwater. Two methods, both practical for application during field trials and full scale implementation across a site, have been developed for generating SOW and delivering SOW in-situ to a target treatment area.

One method utilises a custom built SOW tower which has been designed and commissioned by Golder and a second method utilises venturi. Performance testing of the SOW tower and venturi was conducted to:

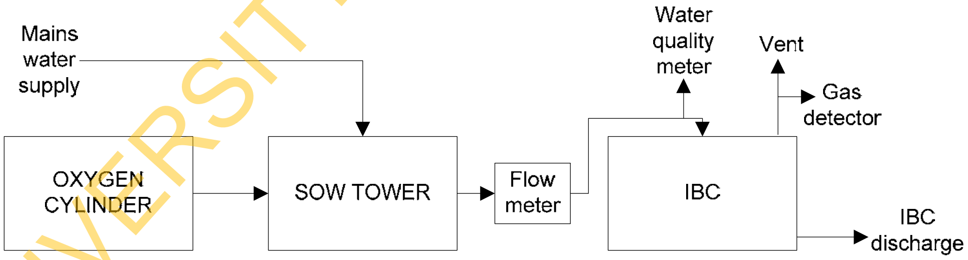
(a) Verify the efficiency of the SOW tower and the venturi in generating SOW
(b) Compare the dissolved oxygen levels in water delivered by the SOW tower and the venturi
(c) Assess and compare oxygen concentrations in atmosphere above the air-water interface

METHODS

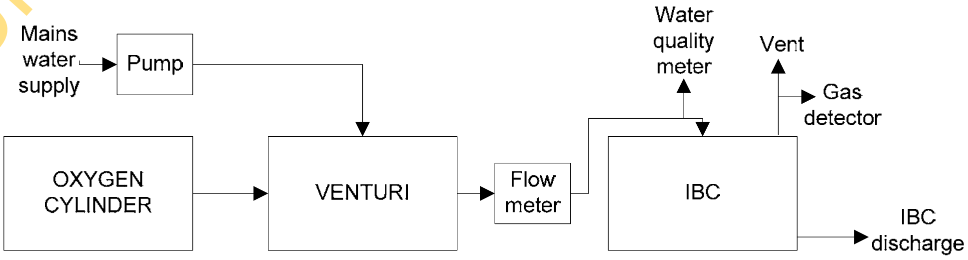
Experiment set up

A test configuration was established to allow direct comparison of the SOW tower and venturi operations. The test configuration involved using a gas cylinder to supply oxygen and mains water supply to either the SOW tower or venturi. The generated SOW was directed into an intermediate bulk container (IBC). Dissolved oxygen concentrations within the SOW were measured using a flow cell and water quality meter. A gas monitor was used to measure oxygen concentrations within the headspace of the IBC.

SOW tower test configuration



Venturi test configuration



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Two staged performance test

A two-staged test was performed with the SOW tower test configuration. The test was repeated with the venturi test configuration. Each test consisted of two stages.

Stage 1 – Rising water level

The Stage 1 test involved increasing the water level within the IBC from approximately 500 litres to 900 litres over a period of 40 minutes. The flow rate of SOW into the IBC was maintained at approximately 12 litres per minute.

Stage 2 – Constant water level

The Stage 2 test involved maintaining the water level within the IBC at approximately 900 litres by allowing water to flow out of the IBC outlet valve. The test was performed for a period of 60 minutes. The flow rate of SOW into the IBC was maintained at approximately 12 litres per minute for the first half of the test and was then increased to 14 litres per minute (SOW tower) and 13 litres per minute (venturi).

RESULTS AND DISCUSSION

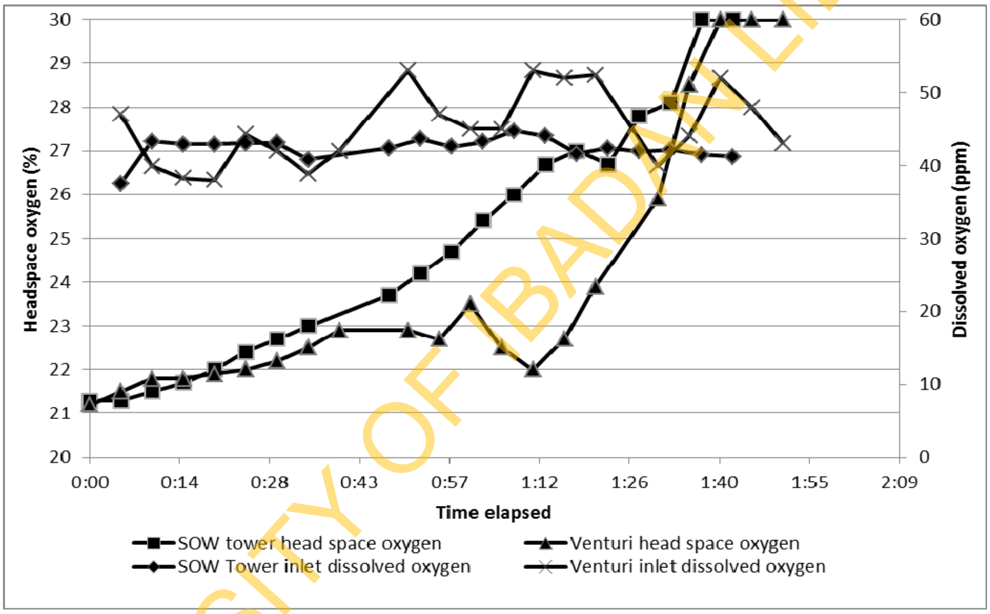

Fig. 1. IBC headspace oxygen concentration and SOW dissolved oxygen content over time for the SOW tower and venturi performance tests.

Results show that the SOW tower produced a most consistent dissolved oxygen concentration in SOW, with higher variability evident in SOW generated by the venturi. This may have be the result of the venturi configuration being more susceptible to fluctuations in mains water supply pressure and oxygen which are by comparison buffered by the volume of the SOW tower vessel.

CONCLUSIONS

The results of the performance tests indicate that both the SOW tower and venturi are able to generate a concentration of dissolved oxygen in SOW in the range of 38 to 53 ppm. For comparable concentrations of dissolved oxygen in SOW for each of the test configurations, the oxygen concentration within the IBC head space was also comparable for the SOW tower and venturi during the two-staged performance tests.

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RECENT DEVELOPMENTS IN IDENTIFICATION OF UNKNOWN CONTAMINATION SOURCES AND MONITORING NETWORK DESIGN FOR CONTAMINATED GROUNDWATER SYSTEMS

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INTRODUCTION

In order to design an effective aquifer contamination remediation strategy two important steps are: (i) identification of unknown groundwater pollution sources once contamination is detected in an aquifer, and (ii) efficient and effective monitoring of contaminant plume movement. James Cook University, Australia and CRC-CARE are collaborating in developing comprehensive and easy to use computer software and state of art methodologies that at can be utilized for (i) identification of unknown pollution source magnitudes, location, and time of activity; (2) optimal design of a contamination monitoring network that can be implemented in any contaminated groundwater site incorporating site specific information. One part of the collaborative research between James Cook University team and CRC-CARE has resulted in the development of software that enables water resources managers and engineers to solve the difficult problems of identifying sources of pollution in a contaminated groundwater systems, and to design optimal monitoring networks that can detect the extent and movement of contaminants in contaminated groundwater systems. The developed computer software make it possible for practitioners with limited knowledge of hydrogeology and pollutant transport processes to address the source identification issue. These software are expected to be immensely useful for proper management of contaminated sites with unknown sources of contamination. The capabilities of the two developed software, the contamination source identification and the monitoring network design, are briefly introduced. Figure 1 shows the architecture of the two developed software packages.

There are various challenging issues that make the source characterization problem very difficult to solve. Some of the complexities arise due to uncertainties in modelling the aquifer system and the associated physical processes, due to sparsity of measurement data in typical contaminated aquifers, due to errors in field measurements, and due to difficulty in predicting the complex geochemical processes involving reactive chemical species such as those occurring in mine sites, and also due to the non-uniqueness of the aquifer response to various stresses i.e., contaminant injection. Few recent advances towards improving the available methodologies are focussed towards making the source identification methodology more versatile and valid under different real-life scenarios e.g., urban spills and abandoned mine sites where very complex reactive geochemical processes are occurring.

The extension of source identification methodology to incorporate complex geochemical reactive environment, incorporation uncertainties through fuzzy quantification, incorporation of uncertainties through Fuzzy quantification, use of Fractal Singularity Index to delineate potential pollution plumes, development of new surrogate or meta models for ensuring the computational feasibility of the developed methodologies are some of the recent advances and possible future trends. The current state of development of these methodologies for more accurate and reliable contaminant source identification and the improvements achieved by implementing a designed monitoring network will be presented.

SOURCE IDENTIFICATION AND MONITORING NETWORK DESIGN SOFTWARE

Some of the source identification methodologies for source identification are reported in: Datta et al.(1989); Mahar and Datta (1997 and 2001); Datta et. al. (2009, and 2010); Sreenivasulu et al. (2012); and Jha and Datta (2012). (Amirabdollahian and Datta, 2013) In the source identification software (CARE-GWSID) the linked simulation-optimization methodology is utilized.

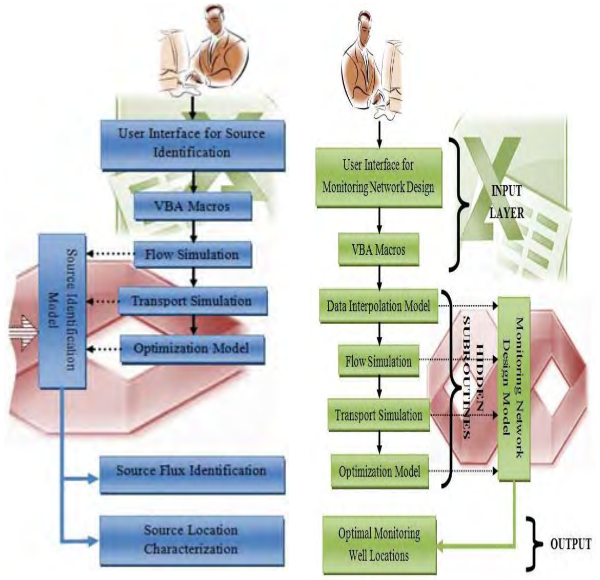


Fig. 1. Software Architectures

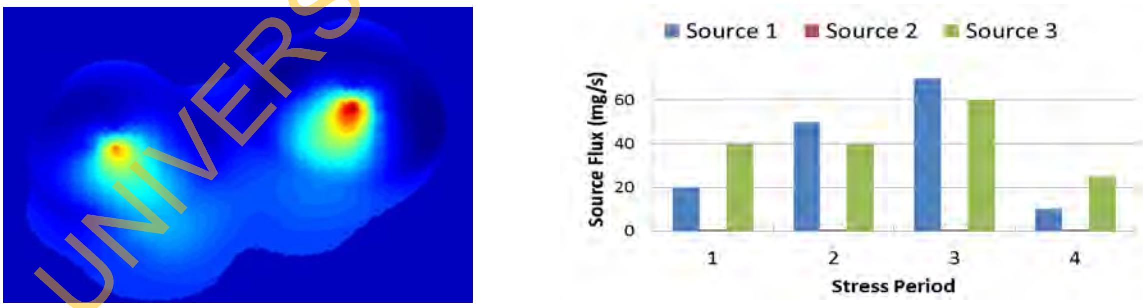
THE MONITORING NETWORK DESIGN SOFTWARE (CARE-GWMND)

A comprehensive UI based software (CARE-GWMND, 2013) for Optimal Monitoring Network Design to address various aspects of groundwater management is developed.. Some of the objectives and methodologies adopted are outlined in Mahar and Datta, (1997), Singh (2008), and Sreenivasulu et.al (2010). (CARE-GWSID manual, 2013).

RECENT DEVELOPMENTS

Some of the recent developments and solution results obtained for complex contaminated sites, i.e., urban aquifers contaminated by leakage of tanks, abandoned mine sites with unknown sources and pathways of contamination exhibiting clear evidence of critical pollution, use of fuzzy quantification of modelling uncertainties to address errors and uncertainties in describing the aquifer system and processes, and some results obtained from validation study of some of the developed methodologies will be presented and discussed.

Figure 2a shows a contaminate aquifer and the pollution plume. The candidate contamination source locations are marked in Figure 2a. Figure 2b shows the estimated source fluxes for each of the candidate source locations using the developed software. Solution results show that the contamination sources are identified satisfactorily.



(a) (b)

Fig.2. Contaminant aquifer; a) Pollution plume, b) Contamination source characteristics.

Source identification and pathway determination for a contaminated mine site in Queensland and in Northern territories, was also carried out, with surrogate models based on Genetic programming and also Self Organizing Maps were developed. These sites also represent complex geochemistry. The source identification exercise will be described for these sites with reactive or radioactive chemicals.

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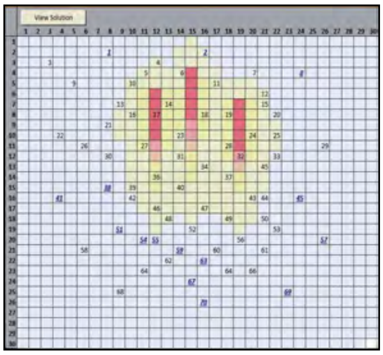

Fig. 3. Selected Monitoring Wells Delineating the Plume Boundary

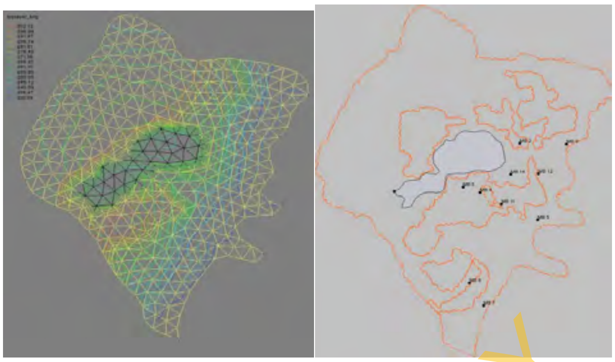

Fig. 4. a) Model definition, b) observation wells location for the mine site aquifer

CONCLUSIONS

Recent developments, future trends and potential use of developed dedicated software related to unknown pollution source identification in contaminated aquifers are discussed. The utility and application of the user-friendly software for source identification and design of effective and economically efficient monitoring network are presented. The extension of source identification methodology to incorporate complex geochemical reactive environment, incorporation uncertainties through fuzzy quantification, incorporation of uncertainties through Fuzzy quantification, use of Fractal Singularity Index to delineate potential pollution plumes, development of new surrogate or meta models for ensuring the computational feasibility of the developed methodologies, are some of the recent advances and possible future trends. The current state of development of these methodologies and some the application results are discussed.

REFERENCES

CARE-GWMND User Manual (2013). Groundwater Monitoring Network Design Software, (Datta et. al.) School of Engineering & Physical Sciences, James Cook University, Townsville, QLD 4814, Australia.

CARE-GWSID User Manual (2013). Groundwater Contamination Source Identification (Datta et. al.), School of Engineering & Physical Sciences, James Cook University, Townsville, QLD 4814, Australia.

Datta, B. et al. (1989). Development of an expert system embedding pattern recognition techniques for pollution source identification. Technical Report. Department of Civil Engineering, University of California Davis, USA.

Datta, B. Chakrabarty, D. and Dhar, A. (2008). Optimal dynamic monitoring network design and identification of unknown groundwater pollution sources. *Water Res. Man.* 23(10):2031-2049.

Jha, M. and Datta, B. (2012). Three dimensional groundwater contamination source identification using adaptive simulated annealing. *J. Hydro. Eng.* 18(3):307-313.

Mahar, P.S. and Datta, B. (1997). Optimal monitoring network and ground water pollution source identification. *J Water Res. Plan. Man.* 123(4):199-207.

Prakash, O., and Datta, B. (2012). Sequential optimal monitoring network design and iterative spatial estimation of pollutant concentration for identification of unknown groundwater pollution source locations. *Environ. Monit. Assess*. 185(7).

Sreenivasulu, C., Datta, B., and Naidu, R. (2012) Optimal identification of groundwater pollution sources using feedback monitoring information: a case study. *Environ. Forensics*. 13(2):140-153.

ANALYTE ION DETECTION METHOD AND DEVICE (probeCARE^{TM})

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INTRODUCTION

CRC CARE has developed a novel technique for the real-time measurement of metal ions in solution using Ion Selective Electrode (ISE) Arrays. The technique includes software that has been developed to allow real-time measurement of a multitude of free ions simultaneously in solution. probeCARE™ allows common ions such as sodium, potassium and calcium to be measured in complex solute matrices, even in coloured solutions. This is of value to agricultural irrigators and for monitoring water quality in lakes and streams. Existing techniques utilise laboratory equipment whose size and weight render them inappropriate for in-field measurements. Consequently, process time and equipment costs can be prohibitive. probeCARE™ supports cost-effective, *in situ*, real-time monitoring , together with improved management strategies for cropping, improved fertigation (applying fertilisers or other soil amendments through an irrigation system), effective use of recycled water, and monitoring for possible pollutants to ensure EPA standards are achieved. probeCARE™ is being developed with internet connectivity to truly support remote sensing and continuous monitoring of critical resources. The technology is at an early stage of commercialisation.

METHODS

In this study, a solid contact ISE array, based on a Prussian blue modified Carbon Paste Electrodes (PB-CPE), was applied with a novel chemometric strategy. One of the most popular Independent Component Analysis (ICA) methods, the fast fixed-point algorithm for ICA (*fast*ICA), was implemented by the Genetic Algorithm (*genetic*ICA) to avoid the local maxima problem commonly observed with *fast*ICA. This *genetic*ICA can be implemented as a data preprocessing method to improve the prediction accuracy of the Back-propagation Neural Network (BPNN). The ISE array system was validated using 20 real irrigation water samples from South Australia, and acceptable prediction accuracies were obtained. Furthermore, instead of using BPNNs, we developed and patented some mathematical models to describe the based characteristics of the ISE array's response, including the sensitivity and selectivity. The developed mathematical equations can be used to simulate the response values of ISE array, and to determine the analytes' concentrations from unknown samples. By measuring only a couple of standard solutions, which is practical to the end users, the ISE array can be automatically recalibrated using Genetic Algorithm (GA).

RESULTS AND DISCUSSION

The sodium potassium adsorption ratio (SPAR) values were calculated and compared using the concentrations from ICP-OES and predicting results from *genetic*ICA_BPNN (Fig.). Since most of the prediction results for Ca and Mg were lower than ICP-OES, it was expected some of the predicted SPAR values would be higher than ICP-OES. It can be seen in Fig. 6 that most of the water samples have no or moderate sodium hazard according to [37]. Two samples were located in the severe hazard cluster. These two samples are recycled water and therefore amendments should be applied for irrigation before they can be used. Only one recycled water sample collected from an artificial lake was not suitable for irrigation based on its SPAR value. The MRE between BPNN prediction and ICP-OES was 23.8% and 95% CL was 32.2%.

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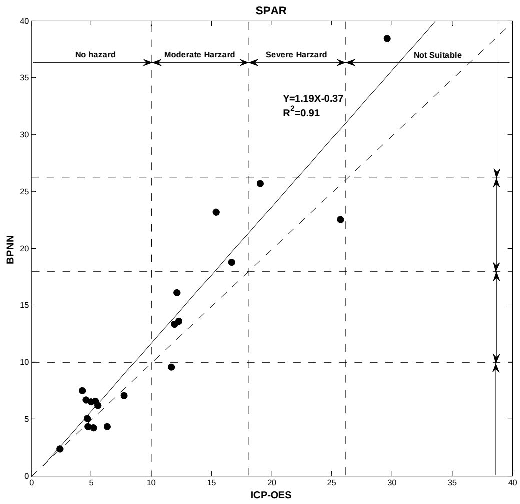

Fig. 1. Predicted results vs. ICP-OES for SPAR of 20 different real water samples (1:1: dash line, regression: continuous line)

Table. The characters for the ISEs

ISE	Sensitivity[1]	Stability[2]	Repeatability[3]	Reproducibility[3]	PRR[4]
Na^+	50.7	8.5	0.14	2.09	14.95
K^+	51.8	6.3	0.07	2.19	15.06
Ca^{2+}	24.3	9.1	0.18	3.38	18.86
Mg^{2+}	23.1	8.9	0.17	3.53	19.26

[1] Unit: mV/dec
[2] % of the decrease of sensitivity
[3] % of Variance based on ANOVA Gauge R&R analysis
[4] % of Gauge R&R of total variations

CONCLUSIONS

After being validated with 20 real irrigation water samples derived from South Australian winery and urban areas, it can be concluded that by using only a small number of calibration samples, this ET system was still able to simultaneously determine the four exchangeable ions with acceptable prediction accuracies. The concentration ranges for the training samples should be able to adjust according to the irrigation water conditions. The narrower the training range, then the more accurate will be predicting the SPAR value. Since the main irrigation source in South Australia is underground water (bore water), the water conditions vary from bore to bore, based on the depth and location. Giving a wider concentration training range is more practical for South Australia. Furthermore, since KNO_3, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ are popular fertilizers, this system can also be used to monitor K^+, Ca^{2+} and Mg^{2+} nutrients in some fertilizer applications.

REFERENCES

L. Wang, D. Yang, C. Fang, D. Lamb, P. J.Lesniewski, M. Megharaj, and R. Naidu, Application of neural networks with novel re-calibration methodologies to a Prussian blue modified Carbon Paste Electrode array for simultaneous determination of nitrate and chloride, Chemometrics and Intelligent Laboratory Systems 144 (2015) 24–30

L. Wang, D. Yang, C. Fang, Z. Chen, P. J.Lesniewski, M. Megharaj, and R. Naidu, Simultaneously determinate four exchangeable cations based on a Prussian Blue Modified Glassy Carbon Electrode array, Talanta131(2015)395–403

EVALUATION OF STATISTICAL AND GEOCHEMICAL METHODS FOR DISTINGUISHING SOIL CONTAMINATION FROM BACKGROUND CONCENTRATIONS

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INTRODUCTION

Understanding background concentrations of common soil contaminants is an essential part of contaminated land assessment. It is important to be able to distinguish contaminated areas from uncontaminated areas and provide a record of the present condition of the environment, to which future changes can be compared (Galuszka, 2007).

This project included a critical evaluation of statistical and geochemical methods to distinguish two soil samples from a vineyard with added copper, from background samples collected from similar parent material.

METHODS

Soil samples (n=104) were collected from Greater Melbourne and the Mitchel Local Government Area, from weathered Newer Volcanics, at depths of 0-10 cm and 30-60 cm. Samples were collected from areas of low disturbance, away from point sources of contamination including roads and industry. Two samples were collected from a vineyard, where copper based fungicides had been used.

A range of common statistics and less common geochemical normalisation and multivariate analysis methods were applied to distinguish contaminated samples from background concentrations. The methods applied included:

(a) 97.5th percentile
(b) Visual assessment of a change in gradient in a cumulative probability plot (CPP)
(c) Median ±2 Mean Absolute Deviations
(d) Upper whisker of a box plot
(e) Geochemical normalisation methods
(f) Principal component analysis (PCA)

The PCA included development of an outlier plot using the variables organic matter, Mn, Cu, Fe, Al, pH and cation exchange capacity. The Mahalanobis distance (which measures the number of standard deviations of a sample result from the mean of a distribution), was used to identify outliers. Statistics were undertaken on both untransformed and log transformed data. The strengths and weaknesses of each method were reviewed.

RESULTS AND DISCUSSION

Background Cu concentrations ranged from <2 mg/kg to 50 mg/kg. The concentration of Cu within the vineyard samples was 48 mg/kg at 0-10cm and 42 mg/kg 30-60cm.

The dataset was positively skewed and did not meet formal parametric requirements of log normal or normal distribution (Figure1a). Log transformation of data resulted in reduced emphasis on elevated results, reducing the capacity of the 97.5th percentile, the CPP the box plot (Figure 1d) and geochemical normalisation method to identify contaminated samples.

The outlier plot accurately identified the two vineyard samples as outliers and also indicated five other samples as chemically dissimilar to the background sample set (Figure 1b).

A loading plot, created using PCA, was useful tool to gain a understanding of which soil parameters were likely to be closely associated with Cu concentrations. Figure 1e shows Fe and Cu to have very similar influence on the first and second component, indicating that these elements may be correlated. This was supported by the linear regression analysis of Cu against Fe (Figure 1f).

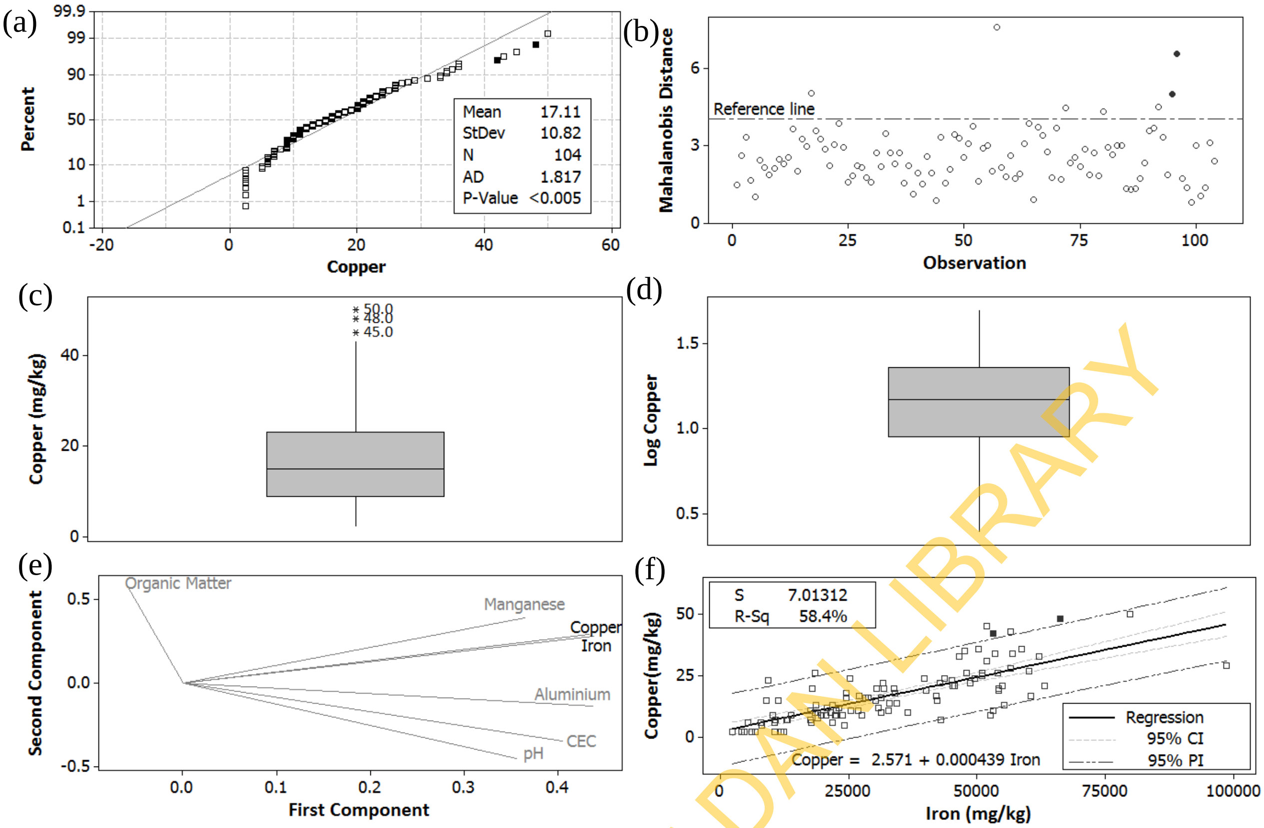

Fig. 1. Statistical methods for identifying samples contaminated with Cu in Newer Volcanic soils from Victoria (a) Probability plot, and Anderson Darling (AD) test of normality, (b) PCA outlier plot, results above the reference line are outliers (c) Box plot, showing individual samples above the upper whisker (d) log transformed box plot, (e) PCA loading plot, (f) geochemical correlation of Cu against Fe, with 95 % prediction interval used to identify outliers. The vineyard samples with elevated Cu are shown as filled symbols

The ability for the varying methods to distinguish both vineyard samples from the background data set are summarised in Table 1.

Table 1. Summary of adequacy of methods to identify contaminated samples

Method	Method identified both contaminated samples
97.5th percentile	No
Median ±2 (MAD)	Yes
Box plot	No
Log transformed box plot	No
Cumulative Probability Plot	Yes
Geochemical normalisation with Fe	Yes

CONCLUSIONS

Typical statistical methods (97.5th percentile, Median ± MAD) are less reliable or informative compared to graphical display of outliers using PCA, geochemical normalisation plots or CPP. However these methods may also identify background samples as potentially contaminated (requiring further evaluation). Box plots may not identify contamination where other elevated results are present, or when data is not appropriately transformed.

REFERENCES

GALUSZKA, A. 2007. A review of geochemical background concepts and an example using data from Poland. *Environmental Geology,* 52**,** 861-870.

THE USE OF CONTAMINANT MASS FLUX AND MASS DISCHARGE TO SUPPORT GROUNDWATER REMEDIATION AT A HISTORICAL GASWORKS, BARANGAROO, SYDNEY AUSTRALIA

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INTRODUCTION

The calculation of contaminant mass flux and mass discharge at Barangaroo, Sydney Australia has been undertaken to support approval of the proposed remediation approach. Sub-surface conditions at Barangaroo are geologically complex, the site being located on the edge of Darling Harbour and having been progressively developed and reclaimed for the past 120 years. Contamination at the site including petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) is derived from a former gasworks facility and historical filling practices. The contaminant mass is located within the fill and marine sediments that underlie the site. Development of a remediation strategy at a site like Barangaroo is dependent upon understanding the distribution of contaminants across the site and the dissolved mass flux or load of contaminants from contamination source zones that might impact sensitive receptors.

Mass flux modelling has been undertaken as one line of evidence to demonstrate that the proposed extent of remediation will result in a reduction of risk to the environment. The objective of the contaminant mass flux and mass discharge calculations at the site is to provide a quantitative approach that demonstrates whether or not:

(a) the contaminant flux from material that (based on the currently proposed extent of remediation) is proposed to remain *in-situ* will be minimal and not represent an unacceptable risk to the environment; and

(b) there will be an improvement in groundwater quality as a result of the proposed remediation.

Remediation is proposed to compromise of either excavation or *in-situ* remediation of soil contamination (predominately within fill material) that is considered to represent an unacceptable risk to human health or the environment. It is proposed that some contamination within the fill and marine sediments (largely west of the historic gasworks) will remain *in-situ*.

CONCEPTUAL MODEL

The works described within this paper are located within the Barangaroo South Area at the location of the former Millers Point Gasworks, operated between 1839 and 1921. The gas works was decommissioned during the period 1922 to 1925 with below ground infrastructure likely infilled with demolition material which was the practice of the day. Waste materials including tars and hydrocarbon contamination were not removed and remain *in-situ* beneath the site. Contamination at the site within soil and groundwater is consistent with contaminants associated with historical gasworks, including monocyclic aromatic hydrocarbons, most notably benzene, PAH including naphthalene, total petroleum hydrocarbons (TPH), heavy metals and coal tar. There is no evidence of contamination within the sandstone bedrock. Lithological conditions are variable across the site, but generally comprise fill material variably overlying sandy clays, clays and marine sediments which directly overlie weathered Hawkesbury Sandstone bedrock. Immediately beneath the former gasworks footprint, the marine sediments are absent but are present down gradient towards Darling Harbour.

Groundwater is present as an unconfined aquifer approximately two metres below the existing ground surface within the fill, marine sediments and Hawkesbury Sandstone, discharging into Darling Harbour. Groundwater velocity calculated within the clayey marine sediments is very low with contaminant migration velocities likely to be an order of magnitude lower due to natural attenuation (sorption and biological degradation). The fill adjacent to Darling Harbour is flushed by tidal activity and has significantly higher groundwater velocities.

MASS FLUX DISCHARGE MODELLING

Mass flux is a term used describe the mass discharge rate in a groundwater plume in units of mass per time passing across a plume transect. The modelling was conducted using Mass Flux Toolkit V 2.0 developed by GSI Environmental to predict how dissolved groundwater contamination alters down hydraulic gradient spatially and over time. The mass discharge along two north-south oriented transects, linking monitoring wells, representative of the variable lithologies and saturated zones was assessed.

Reduction in Mass Flux

Transect A-A' extends for 250 m through the former gasworks and intersects fill and Hawkesbury Sandstone. The mass flux toolkit was used to estimate the contaminant mass flux for contaminants naphthalene, TPH C_{10} – C_{14} and benzene along Transect A-A' before and after remediation. This was achieved by using existing data for the before case and estimating the outcome post remediation. The contaminant mass flux through the former gasworks footprint estimated a reduction in contaminant mass flux in the order of 250% to 380% following the proposed remediation program.

Mass Flux Entering Darling Harbour

The mass flux toolkit has also been used to calculate whether the contamination remaining *in-situ* following the proposed remediation will not represent an unacceptable risk to the environment based on estimation of the concentrations of contaminants that will enter Darling Harbour. Transect B-B' extends for 275 m west of the former gasworks approximately 45 m east of the foreshore intersecting fill and *in-situ* marine sediments. Dissolved contaminant levels within the fill and upper 5 m of the marine clays along Transect B-B' adjacent to Darling Harbour were conservatively modelled using the highest reported groundwater dissolved contaminant concentrations for naphthalene, TPH C_{10} – C_{14} and benzene. The mass discharge calculations indicated the majority of contaminants (more than 99%) travelling off-site (across Transect B-B') into Darling Harbour will be derived from the fill. Mass flux discharge modelling demonstrated that the residual effect of low mass flux from the fill combined an even smaller mass flux from the marine sediments will, in total, result in low impacts on Darling Harbour.

CONCLUSIONS

Based on the available investigation results and the conceptual site model, contaminant mass flux modelling was used to demonstrate that remediation of marine sediments and sandstone was not warranted. This is because the contaminant mass that would remain *in-situ* following implementation of the proposed remediation methodology and would not pose an unacceptable risk to the environment. The results of the mass flux discharge modelling demonstrated that following removal of the contaminant mass, by the proposed remediation works, the mass flux from contamination remaining *in-situ* (largely west of the historical gasworks) will be such that groundwater released to Darling Harbour will not represent an unacceptable risk to the environment.

ACKNOWLEDGEMENTS

We thank Lend Lease Pty Ltd and AECOM Australia Pty Ltd for permission to publish the outcomes of these hydrogeological investigations and mass flux modelling. At AECOM Brad Eismen is thanked for conducting the initial mass flux modelling and providing technical direction. Michael Jones is thanked for his guidance and reviewing the manuscript. NSW EPA contaminated land site auditor, Graeme Nyland provided valuable input in refining the adopted methodology.

REFERENCES

ANZECC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resourced Management Council of Australia and New Zealand.

CCME 2008; Canada-Wide Standard for Petroleum Hydrocarbons (PHC) in Soil – Table B-9 values for TPH C_{10} to C_{12} and $C_{>12}$ to C_{16}.

RISK BASED LAND MANAGEMENT: WHAT IT IS; WHAT IT IS NOT

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INTRODUCTION

There is widespread agreement that current industrial and waste management activities should not be carried out in a way that will cause the release of potentially dangerous chemicals into soil or water. In Europe this is regulated by instruments such as the Industrial Emissions Directive or Environmental Liability Directive. However this presentation focuses on historic contamination where either an existing land use will continue or where a change to a more sensitive land use is considered.

Risk is a product of hazard and receptor vulnerability. A substantial hazard with nothing to harm, or no means of achieving proximity to cause harm, represents no risk. Several policy approaches involving hazard rather than risk based management of historic contamination have been tried in different countries and then abandoned as being unaffordable and not pragmatic.

RISK BASED LAND MANAGEMENT

Risk based land management is not, only, science! RBLM is a process of making decisions in the face of competing interests and great epistemic and aleatory uncertainty. It is about ensuring that human health and the environment are protected; past errors are corrected and land is rendered safe for its future use. Historic contamination is a feature of any industrialising, industrialised and even post industrialised country. Contamination is also naturally occurring in both industrialised and non-industrialised areas within a given country.

But what is the alternative? The alternative is either hazard elimination or an arbitrary legal standard. Both have been tried and both have been found wanting. Hazard elimination is both unnecessarily expensive and at times technically impossible to achieve and always impossible to demonstrate - chemical analyses have reporting limits after all. Strict legal limits are easy to enforce but are sometimes not safe enough and at other times overly conservative and therefore difficult to achieve. Society has in many cases decided what level of toxicological risk it is able or prepared to accept. Societies do this by setting or adopting air quality or drinking water standards. In the realm of the toxicologist the limit of tolerability is clearly defined. However we dwell in the realm of the soil and look at risk through the lens of daily or, as in the case of asbestos, cumulative exposure.

So the challenge is to ensure decisions on whether or not to remediate are taken on the basis of sufficient and relevant information while always seeking to err on the side of caution when it comes to allowing our fellow citizens to live on any given piece of land.

ASSESSMENT CRITERIA

Staged risk assessment is widely recognised as being cost effective. A qualitative assessment based on historical information and site walkover can inform a conceptual site model (CSM). Uncertainties in the CSM are resolved by intrusive site investigation. Soil contaminant concentrations are evaluated by comparison to relevant soil assessment criteria protective of human health, water quality or ecology as appropriate. Generic criteria based on exposures representing minimal or negligible risk to human health can help rapidly screen out contaminants from further consideration and thereby speed up the evaluation process by focusing attention on those contaminants exceeding such criteria or for which no criteria have been developed. Site specific criteria that better reflect site specific soil or contaminant conditions or toxicological information more relevant to the legal situation are used to determine the need for remediation. However throughout, the numerical values being must be considered alongside context specific meta-date: “numbers alone are not enough” (Harbicht II).

SUSTAINABLE LAND MANAGEMENT

The stewardship of soil resources and the management of land use activities are key policy objectives of the European Union. Mark Twain is quoted as advising “Buy land, they’re not making anymore”. Although not strictly true, land is in limited supply. A move to circular land use management is being made – looking at development not as an endpoint but as a stage in a cradle-to-grave-to-cradle cycle of using land for a series of purposes over time. Such an approach can help minimise urban sprawl, protect scarce productive soil and maintain urban systems. Understanding urban systems in terms of their environmental, social, economic and governance performance is an essential part of sustainable urban land management.

“Sustainable brownfield regeneration is the management, rehabilitation and return to beneficial use of brownfields in such a manner as to ensure the attainment and continued satisfaction of human needs for present and future generations in environmentally sensitive, economically viable, institutionally robust and socially acceptable ways within the particular regional context” (RESCUE 2005). The EU FP7 HOMBRE project has proposed decoupling the land use and land use management cycles to generate concurrent activity and minimise the time land is left unused or underused. CABERNET (2006) recognised that brownfield sites do not necessarily need to be affected by contamination. This can be determined at the qualitative risk assessment stage.

RISK COMMUNICATION

Effectively appreciating and the addressing stakeholder concerns is time consuming and at times costly. Failure to do so, can destroy value and impede, or greatly slow down, land development. Transparency, objectivity and robustness are ingredients in fostering trust and ensuring acceptance of the outcomes of risk based land contamination management (CRC CARE 2010; NICOLE 1998; US EPA 1988).

CONCLUSIONS

Risk based land contamination management has an important contribution to make in broader sustainable land management. Ensuring land is suitable for use and effective risk communication are essential prerequisites to that contribution being effective.

REFERENCES

CABERNET (2006) Sustainable Brownfield Regeneration: CABERNET Network Report. ISBN 0-9547474-5-3

CRC CARE (2010) Engaging the community: a handbook for professionals managing contaminated land L. Heath, S.J.T. Pollard, S.E. Hrudey and G. Smith, Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, March 2010, 90pp.

RESCUE. 2005. Best Practice Guidance for Sustainable Brownfield Regeneration. Edwards, D., Pahlen, G., Bertram, C. and Nathanail, C.P. Land Quality Press on behalf of the RESCUE consortium, Nottingham. ISBN 0-9547474-0-2

HOMBRE (2014) HOlistic Management of Brownfield Regeneration: Urban Land Management 2065. http://tinyurl.com/ponjtlk accessed 2 August 2015

NICOLE (1999) Communication on contaminated land. Network on Industrially Contaminated Land in Europe http://www.nicole.org/uploadedfiles/2004-communication-contaminated-land.pdf Accessed 2 August 2015

US EPA (1988) Seven cardinal rules of risk communication http://www.epa.gov/care/library/7_cardinal_rules.pdf Accessed 2 August 2015

SUSTAINABLE DEVELOPMENT OF BROWNFIELDS

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INTRODUCTION

Since its inception in 1995, EPA's Brownfields Program has grown into a proven, results-oriented program that has changed the way contaminated property is perceived, addressed, and managed. EPA's Brownfields Program is designed to empower states, communities, and other stakeholders in economic redevelopment to work together in a timely manner to prevent, assess, safely clean up, and sustainably reuse brownfields. A brownfield is a property, the expansion, redevelopment, or reuse of which may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminant. It is estimated that there are more than 450,000 brownfields in the U.S. Cleaning up and reinvesting in these properties increases local tax bases, facilitates job growth, utilizes existing infrastructure, takes development pressures off of undeveloped, open land, and both improves and protects the environment. Through passage of the Small Business Liability Relief and Brownfields Revitalization Act, effective polices that EPA had developed over the years were passed into law. The Brownfields Law expanded EPA's assistance by providing new tools for the public and private sectors to promote sustainable brownfields cleanup and reuse.

GRANTS AND FUNDING

Brownfields grants continue to serve as the foundation of EPA's Brownfields Program. These grants support revitalization efforts by funding environmental assessment, cleanup, and job training activities. Brownfields Assessment Grants provide funding for brownfield inventories, planning, environmental assessments, and community outreach. Brownfields Revolving Loan Fund Grants provide funding to capitalize loans that are used to clean up brownfields. Brownfields Job Training Grants provide environmental training for residents of brownfields communities. Brownfields Cleanup Grants provide direct funding for cleanup activities at certain properties with planned green space, recreational, or other nonprofit uses. To facilitate the leveraging of public resources, EPA's Brownfields Program collaborates with other EPA programs, other federal partners, and state agencies to identify and make available resources that can be used for brownfields activities. In addition to direct brownfields funding, EPA also provides technical information on brownfields financing matters.

BROWNFIELDS DEVELOPMENT

EPA actively promotes land revitalization. Working in conjunction with government agencies at the local, state, and federal levels, as well as external partners, the Land Revitalization Program supports all stages of the land revitalization process. Whether sharing best practices with the public and government employees, supporting assessments of neighborhoods and properties, or working with communities to envision redevelopment of remediated land, EPA provides tools to facilitate successful results.

SUSTAINABLE DEVELOPMENT

The Brownfields Sustainability Projects are an EPA effort to promote environmental sustainability at local brownfields projects. EPA is providing communities with technical assistance to help them achieve greener assessment, cleanup, and redevelopment at their brownfields. Assistance will support activities such as the reuse and recycling of construction and demolition materials, green building and infrastructure design, energy efficiency, water conservation, renewable energy development, and native landscaping. These projects will also demonstrate best practices that can be used by other communities across the country.

An important strength of brownfield redevelopment has always been its contribution to sustainability. With the growing concern about climate change and greenhouse gas emission control, there has been an explosion of "green building" statutes and ordinances at the state and local level, many of which have impacted brownfields redevelopment. As a result of such general concern and a new legal and regulatory regime, a trend has developed of integrating sustainable building principles into the redevelopment of brownfields. For example, many brownfield projects are being encouraged to reuse the building materials, to retain and manage their stormwater on-site, to conserve energy and water, to install more efficient insulation, and to plant trees. In many jurisdictions, developers can obtain approval of their building plans more quickly if they incorporate sustainable redevelopment principles into their plans. Recently, the focus on environmentally-sound brownfields policy has expanded to include incorporating sustainable environmental practices into the remediation of contaminated sites. Such principles can be implemented long before any "green" buildings are erected on a former brownfields site.

RESULTS AND DISCUSSION

Brownfields Success Stories highlight the accomplishments of EPA brownfields grantees across the country. These accomplishments include transforming brownfields into thriving new centers of commerce and industry; creating jobs through cleanup and reuse; formatting innovative partnerships among federal, state, and local governments and private-sector stakeholders such as developers and lenders; training residents of brownfields communities for high-wage environmental careers; and countless other examples of how brownfields restoration has positively impacted local economies and the quality of life for neighboring communities.

CONCLUSIONS

Revitalizing brownfield sites creates benefits throughout the community, and improves image and overall quality of life. Over 24,000 sites were assessed, and over 1200 sites were cleaned up and land reused for sustainable infrastructure development. Through fiscal year 2014, on average, $17.79 was leveraged for each EPA brownfields dollar invested and 7.3 jobs leveraged per $100,000 of EPA brownfields funds expended on assessment, cleanup, and revolving loan fund cooperative agreements. EPA study also found that residential property values increased by 5.1–12.8% percent once a nearby brownfield was assessed or cleaned up. Private sector invested over $22 billion dollars and created more than 105,000 jobs. Through fiscal year 2014, approximately 50,000 cleaned up acres made available for reuse and infrastructure development.

REFERENCES

WWW.EPA.GOV

INNOVATIVE LNAPL CONCEPTUAL SITE MODEL DEVELOPMENT TOOLS IN SUPPORT OF MORE SUSTAINABLE RISK-BASED LNAPL SITE MANAGEMENT

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INTRODUCTION

The management of sites impacted by light non-aqueous phase liquids (LNAPLs) has historically focused on the quick implementation of aggressive remedial/recovery techniques to mitigate perceived risks. However, recent LNAPL guidance, as well as years of academic study and empirical data have revealed: 1) How little can actually be accomplished at most LNAPL sites in terms of achieving a marginal change in conditions; 2) That many LNAPL sites do not present the risks that have been assumed historically; and 3) Natural source zone depletion (NSZD) can account for much more significant rates of natural LNAPL attenuation than was previously believed to be possible. With so little potential benefit to be realized by LNAPL remediation in many cases, focus is shifting toward a more sustainable risk-based paradigm of LNAPL site management. This new paradigm is anchored by a decision-making process that gives much more weight to remediation risk and environmental impacts that have not been typically considered. For example, a serious consideration of the risks generated by and environmental emissions associated with more traditional LNAPL remedial efforts would undoubtedly lead to a shift from active power and resource-intensive remedial techniques to more passive and more sustainable approaches. This new paradigm is made possible, in part, by modern site characterization techniques that have allowed much more certainty in developing the LNAPL Conceptual Site Model (LCSM) and validating that more passive and more sustainable approaches can be appropriately protective of human health and the environment and are also much more likely to result in an overall environmental benefit. Perhaps most importantly for Australia, the use of innovative site characterization methods and the net environmental benefit approach to LNAPL site management to be explored in this presentation feature prominently in CRC-CARE's recently released Technical Report No. 34, *A Practitioner's Guide for the Analysis, Management and Remediation of LNAPL* (February 2015). GHD has similar experience in Australia, where aggressive remediation has not always produce acceptable results within reasonable cost and time frame.

METHODS

The presentation will compare and contrast the investigative approaches and remedial costs at two sites involving large, complex LNAPL bodies that were characterized using innovative techniques including laser-induced fluorescence (LIF) surveys, LNAPL transmissivity evaluations, soil core petrophysical testing and three-dimensional visualization of resulting data. At Site 1, a large-scale aggressive LNAPL recovery system was implemented, whereas a more passive sustainable approach is to be implemented at Site 2. Site conditions at both sites were comparable: LNAPL was stable, potentially mobile/recoverable fractions were low, and there were no unacceptable exposure scenarios. Two simple approaches to net environmental benefit analysis were applied to the remediation system operating at Site 1 using US EPA's eGRID emission factors and Spreadsheets for Environmental Footprint Analysis (SEFA) in order to contrast the potential benefits with the costs of the activity.

RESULTS AND DISCUSSION

The simple net environmental benefit analysis applied to the remediation system operating at Site 1 exposed the substantial disconnect between the actual benefits and costs of the activity. For Site 2, the sophisticated multiple lines of evidence site characterization approach that was implemented led to the approval of a much more passive, sustainable, cost-effective and technically-appropriate approach to LNAPL management than was initially envisioned by regulatory authorities. This resulted in a dramatic reduction in financial and environmental impacts.

CONCLUSIONS

The use of modern site characterization tools allows the development of much more accurate and reliable LCSMs, which in turn lead to site management strategies that are based not on perceived (often incorrectly) risks, but rather on actual risks where present as well as other sustainable considerations. Recognizing the common lack of risk and central role of NSZD at LNAPL sites, the actual environmental benefit of LNAPL remediation can be more realistically scrutinized than it has been in the past, which should go far in preventing the wasteful use of resources on futile cleanup efforts that may create more risk and environmental impacts than could be reasonably mitigated.

REMEDIATION END POINT: RISK BASED OR PUBLIC PERCEPTION? CASE STUDY OF THE REMEDIATION OF A PETROLEUM HYDROCARBON PLUME IN PERTH, WESTERN AUSTRALIA

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INTRODUCTION AND BACKGROUND

Petroleum hydrocarbon plumes are a common occurrence in groundwater in the vicinity of older service stations. This is of particular concern in the sands of the Swan Coastal Plain of Western Australia, where migration downwards through the soil profile and subsequently hydraulically down gradient can be a relatively rapid occurrence. In recent years, remediation has moved beyond ‘remediation for remediation’s sake’ towards remediation on a risk basis – that is, is there an unacceptable risk to human health, the environment or any environmental value based on the site’s land use. But what happens when the threat of negative public perception outweighs the scientific principles of risk assessment? How is an appropriate remediation path determined?

The study site operated as a service station in an outer metropolitan suburb of Perth from 1959 until closure and decommissioning in 2005. It was classified under the Western Australian *Contaminated Sites Act 2003* (the Act) as ‘Contaminated – remediation required’ and as a designated ‘source site’; with four associated ‘affected sites’ classified as ‘Possibly contaminated – investigation required’. Whilst two of these affected sites were road reserve, the others were a fire station and a primary school.

Environmental Strategies (ES) became involved with the site in early 2012, by which point the previously incumbent consultant had completed Phase 1 and 2 investigations (including two groundwater monitoring events) and a human health risk assessment (HHRA). Based on the information known at the time, ES’ original project objective was to complete the characterisation of the nature and extent of the groundwater plume (on and off-site), and impacts at the source site in order to inform a remedial action plan (RAP), and subsequently remediate the source and affected properties to a degree suitable for their current use, and facilitate appropriate regulatory re-classification.

METHODS

To meet the overall project objectives, ES developed a RAP which presented the direct injection of a combined oxygen releasing compound/in-situ chemical oxidation (ORC/ISCO) product (Klozur CR ™) as the most appropriate method of remediation. The ISCO component of the product is designed to actively reduce contaminant mass, whilst the ORC component ameliorates the biodegradation process.

Subsequent to a pre-injection, baseline groundwater monitoring event (GME), between 21st and 23rd October 2013, ES injected 2 tonnes of Klozur CR ™ combined with 8,500L of water across 36 key locations, at and in the vicinity of the source site. The slurry was pumped into the zone of impact via stainless steel probes driven into the target location via a geoprobe drill rig.

As per the requirements of the RAP, post-injection GME’s were undertaken in February 2014, May 2014 and October 2014.

RESULTS AND DISCUSSION

Post injection groundwater monitoring indicated the following:

(a) Order of magnitude reductions in concentration of methyl tert butyl ether (MTBE); and benzene, toluene, ethylbenzene and xylenes (BTEX) were reported in samples from the majority of wells located in and down hydraulic gradient of injection locations;
(b) In spite of these improvements, concentrations of BTEX compounds were identified in excess of domestic non-potable groundwater guidelines in groundwater samples from three wells; and
(c) Concentrations of MTBE remained in excess of domestic non-potable water guidelines at samples collected from five locations.

Originally the objective of the remedial works was to remediate to a point where there were no unacceptable risks to human health, environmental health, or any environmental value (based on individual land uses), in order to facilitate regulator reclassification of the site. ES provided a risk assessment that demonstrated that these remediation goals were reached based on the analytical results of the GMEs. In spite of this, discussion with the regulator revealed that whilst unacceptable risks were not present, there was an expectation that groundwater at the affected sites (in particular the local primary school) would be restored to conditions meeting the domestic non-potable guidelines, a guideline wholly irrelevant based on the conceptual site model, prior to the site being reclassified under the Act. As such, the remediation goal became somewhat more nebulous and was then redeveloped to something much more difficult (and expensive) to meet: to reduce impact concentrations below a demonstrably irrelevant guideline.

CONCLUSIONS

Based on the works undertaken, the following conclusions were made:

(a) Trend analysis indicated generally decreasing trends of chemicals of potential concern at and in the vicinity of the site;
(b) Examination of the plume diagrams indicated that the plume has historically moved in a ‘pulse’ like fashion, with the area of highest concentrations of contaminants of concern moving very slowly down hydraulic gradient, whilst decreasing in concentration overall;
(c) ES considered the site conditions to be generally supportive of both aerobic and anaerobic degradation of petroleum hydrocarbons in groundwater, and anticipated the ongoing decline of contaminant concentrations;
(d) Risk assessment completed by ES indicated that there is no unacceptable risk due to the groundwater impacts identified at the site or affected sites; and
(e) In spite of the above, further remedial activities will be undertaken in order to remediate the site to the level required by the regulator.

REFERENCES

Contaminated Sites Act 2003 (WA), State of Western Australia, Perth.

Department of Environment Regulation (2014) *Assessment and Management of Contaminated Sites, Contaminated Sites Guidelines,* State of Western Australia, Perth.

National Environment Protection (Assessment of Site Contamination) Measure 199, National Environment Protection Council, Canberra.

FIRST APPLICATION OF THE SUPER OXYGENATED WATER (SOW) TECHNOLOGY IN AUSTRALIA: CASE STUDY FOR SANDY SOILS

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INTRODUCTION

SOW is an emerging groundwater remediation technology that has already been successfully tested and implemented in North America and in Europe.

Dissolved oxygen is injected into the groundwater producing concentrations of up to 50 ppm, which is five times greater than the natural dissolved oxygen concentration of background groundwater levels. This creates a reactive zone with high dissolved O_2 concentrations and enough nutrients to degrade hydrocarbons into harmless products.

The SOW technology was applied for the first time in Australia at former service station site in which groundwater was impacted by petroleum hydrocarbons. Those impacts are present in the saturated zone of an unconfined aquifer characterized by the presence of sandy clays and clayey sands. The conditions were considered favourable for the application of SOW.

Prior to the full scale implementation, the SOW technology was tested at the site with the aim to assess the appropriateness of implementing SOW injections as a viable remediation technology. A SOW injection trial assisted with obtaining information in relation to the influence of SOW injections on groundwater levels in surrounding wells and the effectiveness of SOW injections to stimulate biodegradation and therefore accelerate the remediation process.

This paper presents the results of the application of this emergency technology via a recirculation loop system, in combination with traditional hydraulic control measures.

SITE SETTING

The site is currently vacant and was occupied by a service station from approximately 1956 to early 2007. The site is bound to the north by commercial properties and residential properties exist to the east, south and west of the site. The site is currently zoned for low density residential use.

Historical environmental investigations have identified petroleum hydrocarbon impacts in the soil and groundwater on and off site as result of storage and handling of fuels in underground and aboveground storage tanks.

Petroleum related infrastructure, including underground storage tanks, above ground storage tanks, bowsers, fuel lines and drainage systems, were removed from the site between August 2009 and July 2011. Petroleum infrastructure removal works included the excavation, classification and disposal of impacted soils. Following these works, residual soil and groundwater impacts were identified at the site.

Based on investigations undertaken at the site, the impacts to groundwater are extensive. The site is subject to a s53X Environmental Audit in accordance with the Environment Protection Act 1970, which is being carried out by an Environmental Protection Agency (EPA) appointed Environmental Auditor – Contaminated Land.

The site is underlain by Pliocene aged Brighton Group, which consists of fine to coarse sands with some minor poorly sorted gravels and is poorly consolidated.

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METHODS

SOW is aimed to stimulate biological degradation of groundwater and capillary fringe hydrocarbon impacts. The SOW is injected at the site via combination of oxygen saturated water made from mains water and treated groundwater into the aquifer at four up-gradient locations (northern site boundary) and four down-gradient locations (southern site boundary). Groundwater is extracted from a bore positioned offsite, to assist hydraulic control of injected SOW and manage remediation of groundwater impacts without altering the vapour risk profile to occupants of the nearby residential properties. Before being re-injected and saturated with oxygen, the extracted groundwater is treated by filtration through bag filters and granular activated carbons. In addition to SOW injection and hydraulic control, four biosparging wells were installed as an immediately accessible contingency measure, should SOW injection and associated hydraulic control be demonstrated to not be effective at management of the leading edge of the plume.

RESULTS AND DISCUSSION

Evidence of degradation of petroleum compound was observed at the end of the nine weeks SOW injection trial with benzene concentrations significantly in some down-gradient monitoring injections. Future monitoring works will be undertaken to assess changes in natural attenuation parameters (dissolved oxygen, redox, pH, electric conductivity), microbial populations and concentration of chemicals of interest.

The SOW technology is implemented at the site in a sustainable manner with low power consumption, limited water usage and no requirements for sewer discharge. Groundwater extraction assists with the hydraulic control and a generation of a closed recirculation loop where the local impacted groundwater is used to remediate the site.

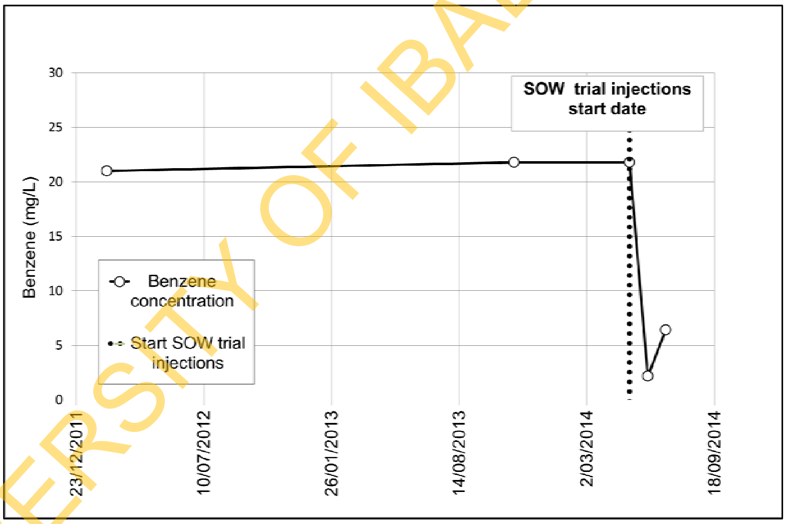

Fig. 1. Benzene concentrations measures at a down-gradient monitoring well, before and after the SOW trial injections.

CONCLUSIONS

The SOW technology has been considered by Golder as innovative and efficient means of achieving remedial end points at the site.

Further monitoring works will be conducted to confirm the efficiency of the selected remedial approach with the aim to progress towards the site closure via the restoration of the beneficial uses.

ACKNOWLEDGMENTS

This project was performed in collaboration with Caltex Australia Petroleum Pty Ltd.

POINT COOK THERMAL DESORPTION REMEDIATION PROJECT

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INTRODUCTION

Enviropacific were engaged by the Commonwealth of Australia (Department of Defence) to undertake the source removal remediation of a former fire training area (FTA) located at the RAAF Williams Base, Point Cook, Victoria (the Site). Historical fire fighting training activities, in particular, were suspected to have tainted the underlying soil and groundwater. With confirmed evidence of contaminated soil and groundwater, a remediation plan (AECOM, 2010) was developed to address the organic hydrocarbon contamination including DNAPL, LNAPL and dissolved phase contamination. During 2014 approximately 70,000 tonnes of highly contaminated soil were treated by ex-situ direct fired thermal desorption technology.

METHOD

In mid-2013 Enviropacific commissioned the manufacture of a direct-fired thermal desorption (DTD) plant for the purpose of treating contaminated soil at the Site. The DTD plant was mobilised to site from the US in late 2013, with installation and commissioning of the plant being completed in early-2014. Proof of Performance (PoP) testing at a feed rate of 23 tonnes per hour was completed successfully in early April 2014 and full scale treatment operations commenced shortly after. Following further optimisation works the DTD operated at up to 30 tonnes per hour and an additional three PoP tests were completed. Treatment activities ceased in February 2015 and the Site has been rehabilitated and revegetated.

Key challenges have included:

- Design and construction of a DTD plant capable of effectively treating high concentrations of chlorinated hydrocarbons;
- Design and construction of general site facilities including water treatment plant, emission control systems, major services including 2 km of underground HV power and water;
- Development of a strong multidisciplinary team capable of managing the project complexity and delivering successful environmental outcomes;
- Commissioning and operation of the DTD plant under an active flight path and close to Port Philip Bay with gale force winds;
- Health and safety considerations when working around highly odourous and volatile hydrocarbons;
- PFOS co-contamination.

RESULTS AND DISCUSSION

This paper will discuss the challenges faced and results achieved in this complex thermal remediation project.

MACDONALDTOWN GASWORKS — AN MGP CASE STUDY

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INTRODUCTION

The Macdonaldtown Gasworks Remediation Site (the "Site") housed a gasworks from 1892 until 1958 which produced gas for the lighting of railway carriages and the Eveleigh Railway Workshops. The processing of coal and shale under heat and pressure to produce the gas created by-products such as tar and ash. These wastes were left on the site when the gasworks was demolished, which was common practice at the time. Over the decades however, the wastes have contaminated site soil as well as groundwater. The contamination sources from the former gasworks infrastructure on the site include retorts, tar and liquor tanks, coal stores, gasholders, boiler houses and purifiers.

Following an Environmental Assessment, RailCorp received approval in January 2013 from the NSW Department of Planning & Environment to remediate the site. The remediation is required under the Contaminated Land Management Act 1997, legislation administered by the NSW Environmental Protection Authority (EPA).

The main contaminants of concern at the site are polycyclic aromatic hydrocarbons (PAHs, including benzo(a)pyrene and naphthalene), total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene and xylenes (BTEX) and small fragments of bonded, non-friable asbestos. Elevated concentrations of heavy metals have also been identified in groundwater.

PROJECT AIMS

The remediation project will help to improve the local environment by:

- Removing contamination caused by the former gasworks operation;
- Improve groundwater quality through monitored natural attenuation (post source removal);
- Preserving the heritage values of the former gasworks; and
- Improving biodiversity via the revegetation of the western portion of the site with locally native species.

PREVIOUS INVESTIGATIONS

In 2014 Thiess was engaged by RailCorp to undertake a Targeted Investigation and Treatment Trial on contaminated soil with the following aims:

- Refine estimates of the volumes and types of soil/material requiring remediation; and
- Determine the most effective treatment methods for site specific soils.

The Targeted Investigation was based on a detailed desktop study and used observations and sampling from excavator trenches, to define the distribution of contaminants at a scale suitable for detailed remediation design. This in conjunction with clean up criteria based on the National Environment Protection (Assessment of site contamination) Amendment Measure 2013 (NEPC, 2013) reduced remediation volumes by up to 40% potentially saving the Client in excess of $8M.

A number of remediation technologies were trialled to treat free tar and tarry soil; including bioremediation, stabilisation/immobilisation and ex-situ chemical oxidation (ESCO). The treatment trial concluded that cement stabilisation for off-site disposal and direct offsite disposal (of some untreated soils) was the most appropriate remedial method for use at the site.

THE PROJECT

The remediation of the site requires the construction of several complex pieces of temporary remediation infrastructure, significant geotechnical and structural works to protect sensitive rail infrastructure, residential properties and the heritage listed ‘Southern Gasholder’ and a robust environmental monitoring programme to ensure the protection of the local community.

The majority of site remediation site will take place within a custom built Environmental Control Enclosure (ECE). The ECE is a single span structure covering over 2600m2 which has been designed to contain emissions of dust, odour and volatile contaminants generated by the excavations. The atmosphere within the ECE will be maintained by a custom built Emissions Control System (ECS) which will filter the air extracted from the ECE.

Excavation within the ECE will be up to 8m below ground level, directly adjacent to the surrounding sensitive structures. A series of retaining walls will be constructed below ground to resist pressure from surrounding earth, support and protect surrounding sensitive structures and serve as a foundation for the ECE.

The Macdonaldtown project has been modelled in its entirety in line using BIM (Building Information Modelling). In the design stage the model has been instrumental in detecting potential clashes between soil nails and sensitive underground structures such as the heritage listed Southern Gasholder and Sydney Water sewer. The model will continue to be developed alongside the progression of the project with the intent being to capture final remediated surfaces and any remaining contamination that must be appropriately managed through the long term EMP. The model will offer significant cost savings to the client as it will allow very detailed and targeted excavation of various waste streams ensuring that material is not unnecessarily sent away for treatment or disposal at a higher class.

COST EFFECTIVE AQUIFER CHARACTERISING TO ACHIEVE CUTEP UTILISING LNAPL TRANSMISSIVITY AND RESIDUAL MASS CALCULATIONS

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INTRODUCTION

Multi-Phase Vacuum Extraction (MPVE) system had been operating at a service station site to remediate Light Non-Aqueous Phase Liquids (LNAPL) from a superficial fractured rock aquifer at regional NSW, under a Voluntary Management Proposal (VMP) with the NSW EPA. Whilst the MPVE system reported significant removal of hydrocarbon mass, several meters of apparent LNAPL thickness remained at certain areas of the site within fractured tuffaceous sandstone.

Limited site characterisation had been completed prior to installation of the MPVE system, with insufficient vertical resolution of the LNAPL plume and an incomplete understanding of the hydrogeological regime and exposure pathways. The objective of the works was to measure a set of parameters that when combined provided multiple lines of evidence to support, or otherwise, the goal of groundwater CUTEP.

Throughout the project the amended NEPC (2013) NEPM was ratified and endorsed by the NSW EPA. The new aspects of the NEPM relating to soil vapour assessment where completed to provide multiple lines of evidence that residual LNAPL did not pose an unacceptable risk to human health and had been removed to the extent practicable. This combined with estimates of LNAPL transmissivity, detailed risk profile characterisation and residual mass calculations allowed a robust estimation of remedial costs to be compared with the potential reduction in risk and a CUTEP conclusion reached.

The project constraints were unique in that the works were all completed based on a truly fixed budget, which if exceeded prior to site closure would be burdened by the consultant. In addition to this all works and findings were subject to review by the appointed NSW EPA Contaminated Site Auditor.

METHODS

To ensure an improved understanding of the site's hydrogeological regime, a detailed assessment was completed. Although the sample collection methods and the equipment used was relatively conventional, the data collected and the manner in which the data was assessed was not. The works included rock coring with detailed fracture logging and PID fracture measurements, multi-staged/levelled monitoring wells, LNAPL baildown tests and transmissivity interpretation, pumping tests at multiple depth zones within the fractured rock and characterisation of underlying beneficial use of the resource aquifer.

An active soil vapour assessment, targeting both on-site and off-site receptors was completed to confirm the hydrocarbon impacted groundwater did not pose an unacceptable risk to human health

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RESULTS AND DISCUSSION

This in-depth assessment of the fractured rock aquifer allowed for the development of multiple lines of evidence demonstrating that the zone of LNAPL impact within the formation was below a perched aquifer, at depth, present under confining pressures, within a low yielding superficial/intermediate aquifer with low transmissivity and storage coefficient properties, and corresponding low LNAPL transmissivity. The results indicating that although the source product was a LNAPL it was present beneath a perched aquifer with separated by a relatively thin confining bedrock unit.

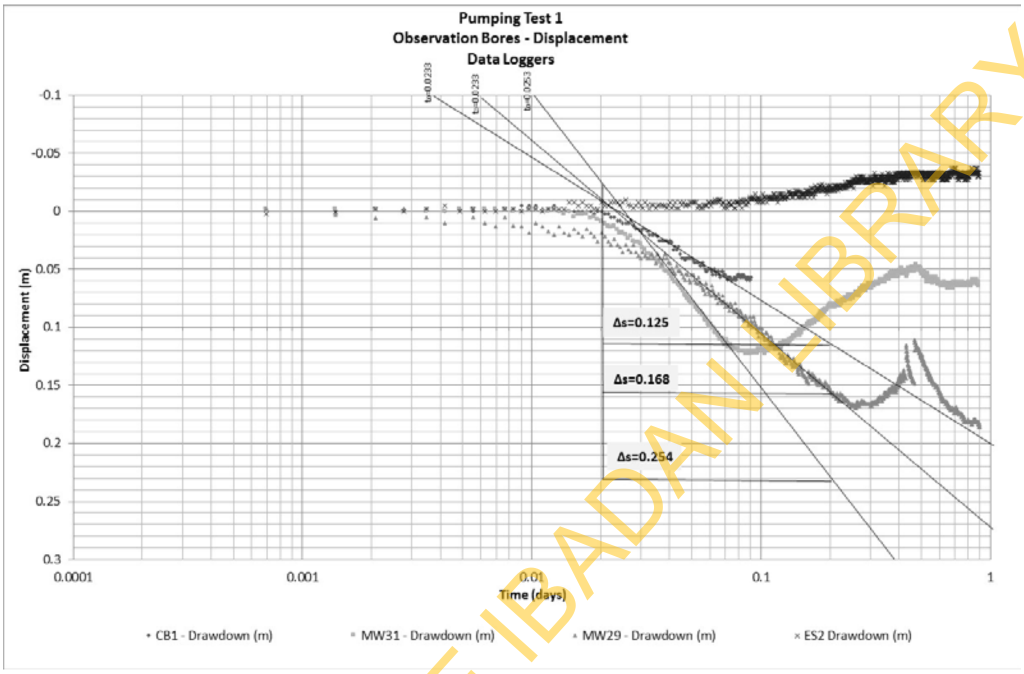

Fig. 1. Drawdown during the low flow pumping test

The results of this work indicated that the remaining mass of LNAPL within the formation was actually limited, with a low transmissivity, and that the only viable exposure pathway was via vapour intrusion. Use of the amended NEPC (2013) NEPM through Tier 1 risk assessment approach (Health Screening Level) indicated that the LNAPL impacted groundwater did not pose an unacceptable risk to human health. By completing this relativity inexpensive hydrogeological characterisation work the MPVE system could have been designed more efficiently, potentially resulting in reduced operational time with significant cost savings and achieving clean up goals earlier

CONCLUSIONS

By completing this relativity inexpensive hydrogeological characterisation work the results indicated that the MPVE system could have been designed more efficiently, potentially resulting in reduced operational time with significant cost savings and achieving clean up goals earlier. Furthermore through the use of relatively conventional sampling techniques and novel data comparisons multiple lines of evidence provided scientific justifications and repeatable metrics to allow a CUTEP conclusion to be achieved.

REFERENCES

Charbeneau, R.J, Kirkman. A, Muthu. R, API LNAPL Transmissivity Spreadsheet: A Toold for Baildown Test Analysis. January 2012.

TC25

DEVELMENT OF TECHNOLOGY FOR REMOVAL OF URANIUM FROM CONTAMINATED SOIL USING INDOOR ELECTROKINETIC DECONTAMINATION EQUIPMENT

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INTRODUCTION

Most nuclear facility sites have been contaminated by leakage of radioactive waste-solution due to corrosion of the waste-solution tanks and connection pipes by their long-term operation, set up around underground nuclear facilities. Therefore it was needed that the method to remediate a large volume of radioactive soil should be developed. In this study, for the reduction of volume of metal oxides generated in cathode chamber, the optimum pH of waste electrolyte in cathode chamber were drawn out through several experiments with the manufactured electrokinetic decontamination equipment. Also, the required time to reach to below the clearance concentration level for self- disposal was estimated through experiments using the manufactured electrokinetic decontamination equipment.

METHODS

The indoor electrokinetic decontamination equipment for treatment of 1.2 tons of contaminated soil per batch was manufactured to remove uranium from lots of soil with high removal efficiency during a short time. The equipment consists of anode chamber, soil cell, cathode chamber, soil cloth sack, pH and pump controllers, an equipment support system, a power supply, gas release cover, and a nitric acid box as shown in Fig. 1. Uranium soil was poured into a soil cloth sack in the soil cell. If the electricity is given at the anode and cathode by the power supply, UO_2^{2+} in the uranium soil moves mainly by electro-migration and electro-osmosis to the cathode chamber.

Fig. 1. Manufactured indoor electrokinetic decontamination equipment

During operation of electrokinetic decontamination equipment, lots of waste electrolyte in the cathode chamber was generated. Waste electrolyte contains lots of metal oxides produced due to metal ions released from the contaminated soil. The volume of metal oxides can be reduced by controlling the pH of waste electrolyte in cathode chamber. Meanwhile, for the reduction of the volume of waste electrolyte being generated in cathode chamber, the waste electrolyte was reused as the electrolyte in the anode chamber. But water or reclaimed solution was used for the last 20 days to elevating the removal efficiency of uranium from soil. The times required for three concentrations of soil to reach to below the clearance concentration level were estimated through experiments using the manufactured electrokinetic equipment.

RESULTS AND DISCUSSION

The percentage of metal oxide volume generated in cathode chamber according to the pH of electrolyte at 25 ℃ was shown in Table1. When the pH of waste electrolyte in cathode chamber increased, the percentage of metal oxide volume generated in cathode chamber increased. Conclusively, it was found that the optimum pH of waste electrolyte in cathode chamber for the reduction of volume of metal oxides was below 2.35. Meanwhile, the electrokinetic decontamination experiments using the manufactured equipment were carried out with maintaining the pH of waste electrolyte in cathode below 2.35 by injecting nitric acid. When the initial uranium concentration of the soils were 20.0 Bq/g,14.0 Bq/g, and 7.0 Bq/g, the required times to reach to below the clearance concentration level for self- disposal were 40 days, 35 days, and 25days as shown in Fig. 2.

Table 1. Percentage of metal oxide volume generated in cathode chamber according to the pH of electrolyte at 25 ℃

	Percentage of metal oxide volume generated in cathode chamber			
pH (25℃)	pH 2.35	3.76	4.16	5.47
Metal oxide volume in chamber	2%	3.5%	70%	90%

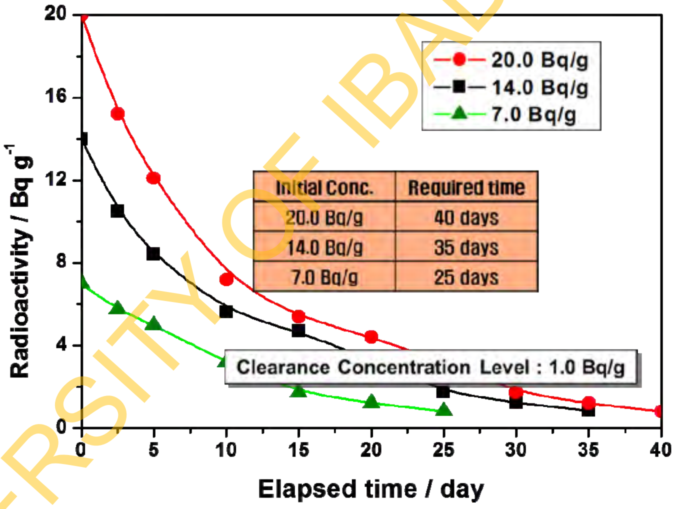

Fig. 2. Uranium radioactivity concentration decrease versus decontamination elapsed time per different initial concentration of soil

CONCLUSIONS

The optimum pH of waste electrolyte in cathode chamber for the reduction of volume of metal oxides was below 2.35. Also, when the initial uranium concentration of the soils were 7-20 Bq/g, the required times to reach to below the clearance concentration level for self-disposal were 25-40days

REFERENCES

Otsuka, K. and Terabe, S.(1989) Effects of pH on electrokinetic velocities in micellar electrokinetic chromatography. J. Microcolumn separations 1(3):150-154.

Kim, G.N., Yang, B.I., Choi W.K. and Lee, K. W.(2009) Development of vertical electrokinetic-flushing decontamination technology to remove ^{60}Co and ^{137}Cs from a Korean nuclear facility site. Separation and Purification Technology 68:222-226.

LONG-TERM BIOEMEDIATION AND MANAGEMENT FOR A CO-MINGLED CHLORINATED SOLVENT AND 1,4-DIOXANE SOURCE AREA AND PLUME

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INTRODUCTION

Historic releases of 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (PCE) at a former industrial facility impacted underlying soil, weathered bedrock, and shallow groundwater. Investigations found that the resultant chlorinated volatile organic compounds (CVOC) groundwater plume extended more than 13,000 feet downgradient of the former facility and was up to 1,200 feet wide and 70 feet deep in certain portions of the site. The principal compound of concern was 1,1-dichloroethene (1,1-DCE), a breakdown product of TCA and, to a lesser extent, TCE. In addition, 1,4-dioxane has been found at moderate concentrations (approximately 100 µg/L) within the footprint of the former facility.

METHODS

A multi-component remedy and site management strategy has been implemented for over 15 years, consisting of hydraulic containment, enhanced in situ bioremediation, monitored natural attenuation, and vapor mitigation.

In the source area, hydraulic containment is being used to prevent contaminants from leaving the site. The treatment system extracts groundwater, removes the chlorinated solvents using an air stripper, reduces the 1,4-dioxane concentration with an advanced oxidation process (AOP), and re-injects the treated water. A residual DNAPL source area (total VOC concentrations as high as 25,000 to 30,000 µg/L) is located beneath a large industrial warehouse that houses an active business.

For the downgradient plume, bioremediation has been implemented in three discrete areas using emulsified vegetable oil injections. The downgradient plume has also caused vapor intrusion concerns for residential areas. Geosyntec implemented a comprehensive indoor air sampling program, with several hundred homes receiving vapor mitigation systems to date. Geosyntec also implements a comprehensive monitoring program to track attenuation of contaminants throughout the remainder of the plume.

RESULTS AND DISCUSSION

The hydraulic containment system has successfully cut off flux of VOC contaminants from the source area to the downgradient plume. Proper operation of the treatment system has eliminated surface water discharges for the last 4 years, saving tens of thousands of dollars in testing, evaluation, and treatment costs. When the AOP component of the treatment system was failing, it was determined that upgrading the system rather than replacing it was feasible, and resulted in a savings of more than $150,000.

The bioremediation injections have been successfully conducted in residential neighborhoods and have resulted in concentration reductions of up to 98% for VOC contaminants. MNA monitoring has shown that VOC concentrations have declined in more than 90% of offsite wells. The indoor air sampling and vapor mitigation program was among the first to be implemented in the state of Colorado, and set precedent for the state approaches vapor intrusion sites.

The presence of 1,4-dioxane limits potentially applicable remediation technologies for the source area. While technologies exist that could treat both the CVOCs and 1, 4-dioxane, evaluation of alternatives has shown that any source remediation would cost significantly more than the present value of several decades of hydraulic containment, primarily due to the difficulty in access caused by the site building. In addition, while remediation could potentially reduce contaminant mass in the source area, it is likely that even after remediation, the hydraulic containment system would still be required.

CONCLUSIONS

Because of the site logistical constraints, the current strategy is to continue operation of the hydraulic containment system with offsite remediation, vapor mitigation, and monitoring.

TOWARDS SUSTAINABLE REMEDIATION IN THE 21st CENTURY: DEFINED MECHANOCHEMICAL REDUCTIVE DEHALOGENATION AT ROOM TEMPERATURE IN A BALL MILL

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INTRODUCTION

1,3,5-Trichlorobenzene (TCB) was completely dechlorinated to benzene in a model reaction with magnesium and n-butylamine *at room temperature in a ball mill*. A full mass balance was observed for its stepwise reductive dechlorination *via* the intermediates 1,3-dichlorobenzene (DCB) and monochlorobenzene (MCB). This mechanochemical (MC) reaction occurred due to ongoing, simultaneous comminution and mechanical activation of small particle size magnesium during milling. The base metal was utilized as the actual dechlorinating agent whereas n-butylamine as a hydrogen donor.

RESULTS AND DISCUSSION

A kinetic study revealed that *consecutive and coupled one-pot* Grignard-Zerewitinoff reactions had occurred: MC activated formations of intermediary Grignard components from 1,3,5-TCB, 1,3-DCB and MCB, took place each first, and then stepwise their protonation to DCB, MCB and benzene, resp., by the amine, which reacted as a (weak) acid towards strongly basic Grignard reagents. A reaction model comprising a corresponding set of rate equations (ordinary differential equations (ODEs) representing an initial value problem) could successfully be fitted to data sets recorded for a representative model degradation reaction of 1,3,5-TCB (Fig. 1). The rate constants for the formation of the postulated intermediary Grignard components were computed, hence this method can readily be extended to determine Grignard formation rate constants in general. Results are in very good accordance to data recently reported for an analogous MC reductive dechlorination reaction of 1,3-DCB and correspond well, too, to other data previously reported.

CONCLUSIONS

In conclusion, MC reductive dechlorination employing base metals *in combination with* hydrogen donors can successfully be applied as a promising non-combustion method to the environmentally friendly, *defined and well characterized* destruction of persistent organic pollutants such as polychlorinated biphenyls (PCBs) or dioxins (PCDD) in the environment at room temperature, thus featuring key elements of emerging sustainable ex situ remediation processes for the 21st century.

REFERENCES

Birke, V., Mattik, J. and Runne, D. (2004) Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants. *J. Mat. Sci.* 39, 5111-5116

Birke, V., Mattik, J., Runne, D., Benning, H. and Zlatovic, D. (2006) Dechlorination of Recalcitrant Polychlorinated Contaminants Using Ball Milling. In: *Ecological Risks Associated with the Destruction of Chemical Weapons, Proceedings of the NATO Advanced Research Workshop (ARW) on Ecological Risks Associated with the Destruction of Chemical Weapons*, Lüneburg, Germany, Series: NATO Security through Science Series, Eds. V.M. Kolodkin and W. Ruck, Springer, ISBN: 1-4020-3136-X, 111-127.

Birke, V., Schuett, C. and Ruck, W.K.L. (2009) Small Particle Size Magnesium in One-pot Grignard-Zerewitinoff-like Reactions Under Mechanochemical Conditions: On the Kinetics of Reductive Dechlorination of Persistent Organic Pollutants (POPs). In: *Environmental Applications of Nanoscale and Microscale Reactive Metal Particles*. Eds: C. Geiger, K. Carvalho-Knighton, Vol. 1027, American Chemical Society, ISBN13: 9780841269927 eISBN: 9780841224674, 39-54

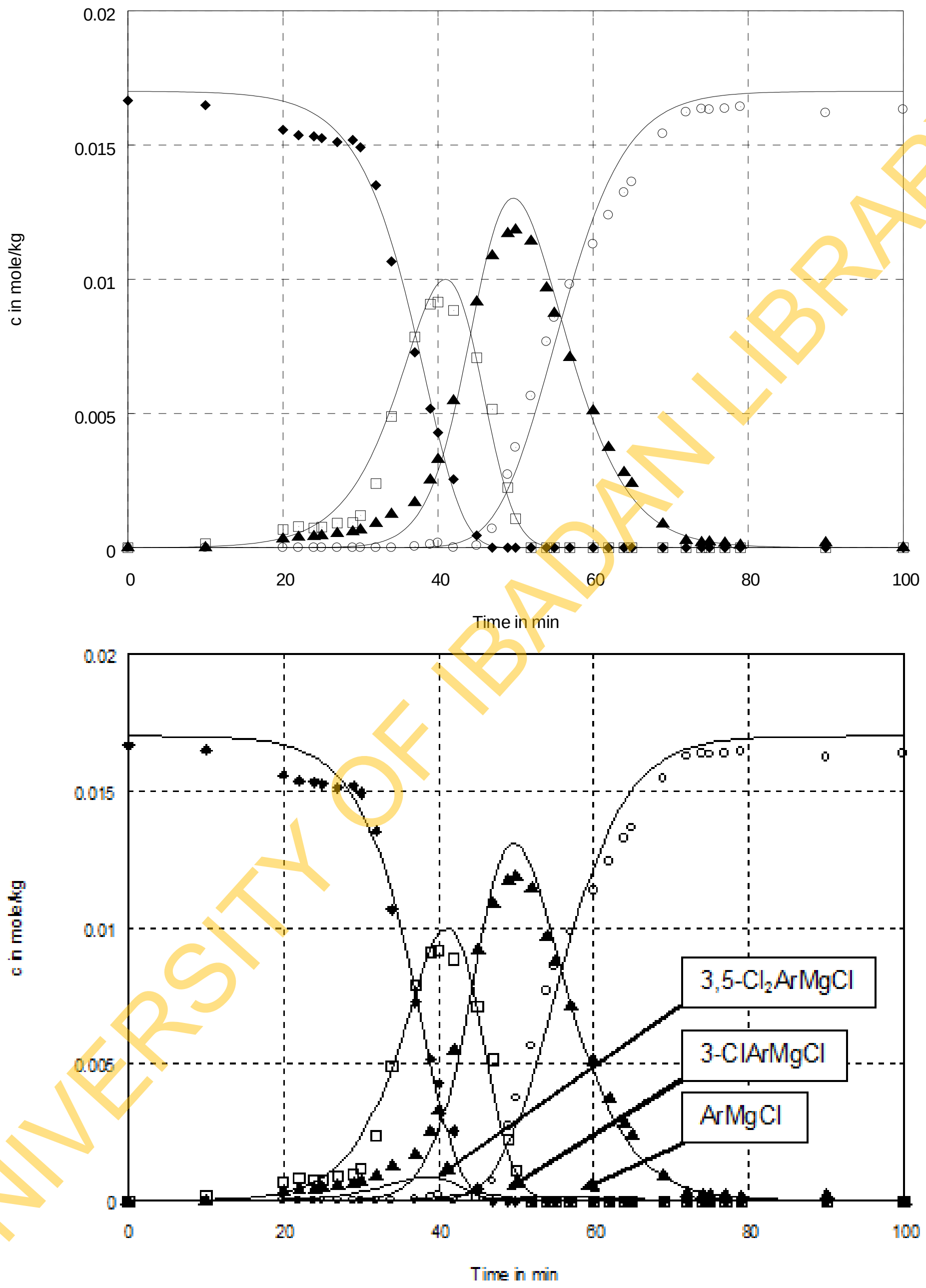

Fig. 1. An initial concentration of 0,017 mole/kg 1,3,5-TCB in sand shows smooth fits for steady state conditions (top) taking into account an estimation of hypothesized Grignard intermediates (bottom) regarding MC reductive dechlorination to benzene. Simultaneous fit of a complete data set covering all analytes to the ODE system, which was derived from the postulated mechanistic scenario, by the least squares routine EASY-FIT. Diamonds denote 1,3,5-TCB, squares 1,3-DCB, triangles MCB, and circles benzene. Both fits are virtually identical and Grignard formation rates and concentrations are estimated, as to be expected for steady state conditions, at low levels.

QUANTIFYING THE MASS OF PETROLEUM HYDROCARON CONTAMINANTS DEGRADED BY MICROBIAL PROCESSES AT AN ACTIVE REMEDIATION SITE

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INTRODUCTION

One of the key performance measures of any active soil or groundwater remediation program is determining the mass of contaminant removed or destroyed by the remediation process. For some methods of remediation this can easily be quantified, particularly when the mass of the contaminant removed can be directly measured. However, where the remediation technology enhances biodegradation, estimation of the contaminant mass destroyed by microbial processes is subject to significant uncertainty. In calculating the contaminant mass removal on active remediation sites, secondary destruction processes such as biodegradation are typically either not acknowledged, or assumed to be a fixed percentage of the estimated contaminant mass removed. As these biologically mediated destruction processes can account for a significant proportion of the contaminant removal, the effectiveness of the entire remediation process can often be underestimated.

This paper aims to quantify the mass removed via biodegradation, and therefore quantify the relative contribution of this 'secondary' process, in order to decrease the uncertainty around percentage hydrocarbon removal.

A better understanding of the contribution of microbial processes to contaminant destruction on petroleum hydrocarbon contaminated sites will provide a more thorough description of the conceptual site model, and therefore allow for optimisation of remediation system operations. Estimation of the mass degraded by biological processes can also provide a valuable line of evidence to support decisions for ceasing active remedial efforts.

METHODS

The site used for this study is a former fuel depot site undergoing active soil and groundwater remediation using a multi-phase remediation approach. The mass of petroleum hydrocarbon contamination removed via physical methods was calculated for the various phases including: Light Non-Aqueous Phase Liquids (LNAPLs), dissolved phase hydrocarbons, and vapour phase hydrocarbons. The mass of hydrocarbons destroyed by microbial degradation was calculated by measuring the carbon dioxide concentrations and air flow rates, and using these values to back-calculate the equivalent mass of petroleum hydrocarbons which has been microbially degraded.

Carbon dioxide was measured at the following locations:

- In an area outside the zone of the petroleum hydrocarbon plume, in order to estimate the background rate of carbon dioxide generation from other organic or inorganic carbon sources,
- Within the vadose zone at variable depths, including measurement of other general gases such as oxygen, and
- At the inlet to the vapour remediation system, as a representative measurement of carbon dioxide flux being removed from the subsurface across the entire remediation well field.

RESULTS AND DISCUSSION

The carbon dioxide concentrations recorded ranged from 0.1% to 2.8%, with the higher readings recorded during remediation system commissioning and system re-start after a period of inactivity. The highest readings were attributed to an initial slug of carbon dioxide

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passing through the remediation system due to a build-up of carbon dioxide in the sub-surface whilst the system was idle.

Several lines of evidence were used to support the conclusion that biodegradation was occurring within the remediation zone, including: measurements of spatial variation in the soil gas composition in the subsurface which corresponded to hydrocarbon impact; comparison of carbon dioxide efflux rates from the literature (McCoy et al, Sihota et al); and microbial plate counts. Background carbon dioxide concentrations were determined by simulating the remediation system operation in a part of the site where no contamination was present. Background carbon dioxide concentrations were recorded at a steady state of 0.5 %.

Based on the recorded carbon dioxide concentrations at the remediation inlet, and subtracting the background concentrations, the mass of petroleum hydrocarbons degraded by biodegradation processes was calculated. These results were compared to the mass of petroleum hydrocarbons destroyed or removed by the active remediation system, Table 1.

Table 1. Comparison of Petroleum Hydrocarbon Mass Destruction by Biodegradation and Active Remediation Processes.

	Petroleum Hydrocarbon Destruction	
	Remediation System	Biodegradation
Lower Bound	0.2 kg/hour	0.3 kg/hour
Upper Bound	1.8 kg/hour	1.4 kg/hour

CONCLUSIONS

When calculating the hydrocarbon mass removed on active remediation sites, the contribution of biological processes such as aerobic biodegradation, are typically either not acknowledged, or assumed to be a fixed percentage of the hydrocarbon mass removed. For the study site, the mass of hydrocarbon removed by biodegradation was estimated to be equivalent to the mass destroyed by the active remediation system.

Recording carbon dioxide and oxygen concentrations can provide valuable information to assist in quantifying the mass of petroleum hydrocarbons destroyed by microbial processes, and also assist with optimising the remediation system operation. Understanding the overall mass of contaminants destroyed or removed can also provide an additional line of evidence to support the cessation of active remedial efforts.

Determining the variability in the flux rate of carbon dioxide across the remediation zone, and the background generation rate of carbon dioxide from other carbon sources, is crucial to enable calculation of reliable estimates of the contribution of biodegradation to contaminant mass removal.

REFERENCES

McCoy, K., Zimbron, J., Sale, T., Lyverse, M., (2014) Measurement of Natural Losses of LNAPL Using CO_2 traps. In: Groundwater. pp. 1-10.

Sihota, N. J., Singurindy, O., Urlich Mayer, K., (2011) CO_2-Efflux Measurements For Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer. In: Environmental Science and Technology. pp. 45: 482-488.

Molins, S., Mayer, K. U., Amos, R. T., Bekins, B. A., (2010) Vadose zone attenuation of organic compounds at a crude oil spill site – Interactions between biogeochemical reactions and multicomponent gas transport. In: Journal of Contaminant Hydrology 112: pp 15-19.

BETTER MANAGEMENT OF REMEDIATION PROCESS UNCERTAINTY

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INTRODUCTION

Remediation projects are complex. The uncertainty in the amount of contaminated material to be remediated and potential risk-based methods to manage this has been a major focus over the last few years. However, one of the other key factors is the uncertainty in the physical remediation process that is required to deliver the project. Improper planning and management of elements such as ground support, access, access to underground utilities, dewatering and the like cannot only lead to significant time and budget over runs but may impact on the feasibility of the adopted remediation method or even the project itself. These issues need to carefully be considered at the assessment and budgeting phases so the optimum remediation option can be selected and properly specified for tender. A recently completed remediation project observed budget exceedences and delays for several project items which has been used to illustrate this issue.

BACKGROUND

Establishing a sound understanding of the remediation process, prior to commencing remediation works is critical as there can be numerous variables and uncertainties encountered which impact on the project. The understanding of how the work is to be done rather than just what needs to be done is a crucial component in preparing a project specification and budget. The time and cost impacts of several items of the remediation project that were not well known at the time of tendering have been considered in this study to illustrate some of these risks.

STUDY FINDINGS

A comparison of the project items that exceeded their original estimate are presented in Table 1. These items have also been assessed against the overall project budget.

Table 1. Cost variation in project items observed on a remediation project.

Project Item	**Percent increase on project item estimate**	**Percent increase on overall project budget**
Excavation volume	19%	8%
Dewatering	350%	5%
Variable fuel price	13%	5%
Availability of temporary utility services	7%	0.3%

An estimate of the total volume of soil requiring excavation and treatment was included in the Schedule of Rates items. This estimate was based on pre-remediation site investigations aimed at delineating the lateral and vertical extent of contamination. The observed volume of soil that was excavated and treated, exceeded the project item estimate by 19%, resulting in an 8% increase to the overall project budget. For this project, the actual variation in remediation volume was low compared to many other sites where 50% or even 100% increases have occurred. This was due to the fact that the area of the excavation was constrained by the project requirements and it was only depth that could vary. Even by removing one of the key uncertainties in volume increases, remediation area, and having a depth generally driven by stratigraphy, small variations in depth lead to the most significant increase in overall project cost. It is likely that this variance could have been better predicted with more focus on the depth as part of the initial volume estimate.

Sheet piles were installed around the perimeter of remediation cells prior to commencing excavation works to allow dewatering systems to be installed. The uncertainty in estimating the volume of groundwater requiring treatment resulted in a 350% increase on the project item estimate and a 5% increase to the overall project budget. This variance was almost as significant as the soil volume variance and could have been avoided through specific studies into likely groundwater volumes and a better allocation of risk to make the contractor responsible for the volumes generated as they were linked to the quality and design of the sheet pile wall installation.

The cost of the fuel used to power the remediation system was priced at the tender stage with a provision for a rate price adjustment to be made in the event the fuel price varied by more than 5%. Fluctuations to the fuel price over the course of the project resulted in a 13% increase to the project item estimate and a 5% increase to the overall project budget. Whilst the project ran through a period of major fuel price fluctuation, the significant risk to the cost on the project budget was not identified at the time of tender.

The remediation method required Contractor access to gas, power and water. Little pre-tender investigation was undertaken to assess how such access would be gained for this site as the services were not available. The cost for provision of services impacted on the tender price. Issues in achieving the access to services post-tender resulted in a 7% increase to the project item estimate and had a minor impact of 0.3% increase to the overall project budget. The cost associated with this item could have been better anticipated and as part of the feasibility assessment for the remediation method for the site.

Excavation works were undertaken inside environmental enclosures, which were often damaged due to 'high winds' resulting in submission of extension of time (EOT) claims and project delays. It is important to understand the project locality and environmental impacts that may affect remediation processes to avoid project delays. The risk of using enclosures in a high wind area could have been better anticipated, costed and the risk better allocated to the contractor prior to the time of tender.

CONCLUSIONS

When developing a budget for remediation projects, the entire remediation process needs to be considered as there may be cost elements that are simply overlooked by focussing on remediation volume and treatment or disposal cost uncertainty. A solid understanding of the actual steps that a contractor must undertake to deliver the remediation is required to be able to identify the main project risks, allocate those risks, create a supportable budget and manage the remaining uncertainty. Such an understanding can be gained by environmental consultants through remediation experience, involvement of contractors in the early period of the works and a greater focus on developing a technical specification for the works at the budgeting stage rather than the more common Remediation Action Plan which focuses on what has to be done rather than how it needs to be done.

ADVANCES IN FIELD SAMPLING: NO-FLOW VERSUS LOW-FLOW

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INTRODUCTION

Low-flow has been an accepted sampling technique for groundwater monitoring in Australia for over a decade. With the recent introduction of no-flow sampling, consultants, and their clients, have been trialling the two techniques in parallel to assess the comparative analytical results. This abstract presents a comparison of analytical results obtained through no-flow and low-flow sampling from twenty locations at a current and a former major hazard facility in Melbourne, Victoria.

The combined data from the sites provides discussion around the benefits and limitations of no-flow versus low-flow sample results, no-flow sampler size, analytical suites and contaminant stratification in long screen wells.

METHODS

No-flow vs low-flow trials were conducted at a current and a former major hazard facility in 2013 and 2014, during annual / biannual groundwater monitoring events (GME).

The primary objective was to compare laboratory results and assess limitations or benefits of no-low sampling. No-flow samplers (HydraSleeve™) were used to collect samples first, followed by low-flow (Micropurge®) to minimise the potential for disturbance of the groundwater level and to reduce the stabilisation time for the no-flow sampling method. HydraSleeve™ samplers are deployed closed and take a discrete sample at the depth of interest using a check valve.

Site A

Ten wells were sampled with both no-flow and low-flow samplers in May 2013. The samples were analysed for the GME analytical suite (TPH, BTEX, naphthalene, total PAHs, lead) using 600 mL no-flow samplers. Wells were selected to cover a range of dissolved phase concentrations from within the plume, plus delineation wells located on the peripheral edge of the dissolved impact.

Site B

Ten wells were sampled with both no-flow and low-flow samplers in December 2014. The samples were analysed for the GME analytical suite (TRH, SVOCs, VOCs, benzene, ethylbenzene, isopropylbenzene, phenols, metals, cyanide, inorganics) using 2 L no-flow samplers. Wells were selected to target the known groundwater impacts and wells with long screens to further assess contaminant stratification. In these, two no-flow samplers were installed in series providing shallow and deep data within the same well and aquifer.

RESULTS

No-flow versus low-flow

No-flow and low-flow results for both sites were plotted and the coefficient of determination (r^2) values indicated that no-flow sampling was a good predictor of low-flow results. The wide range of concentrations across the combined dataset showed that no-flow samples are equally good at predicting low-flow results for low concentrations as for high concentrations. While regression order statistics (calculated using US EPA ProUCL 4.1 software) were utilised to estimate values below PQL for Site A, where concentrations were predominantly low, this method was not required for Site B and has not been utilised in the combined dataset. The no-flow results were predominantly higher than the low-flow results (gradient >1) for the dominant contaminants (example in Figure 1), however no-flow results were generally lower than low-flow for inorganics and metals. Overall, all results were in the same order of magnitude as respective comparative samples.

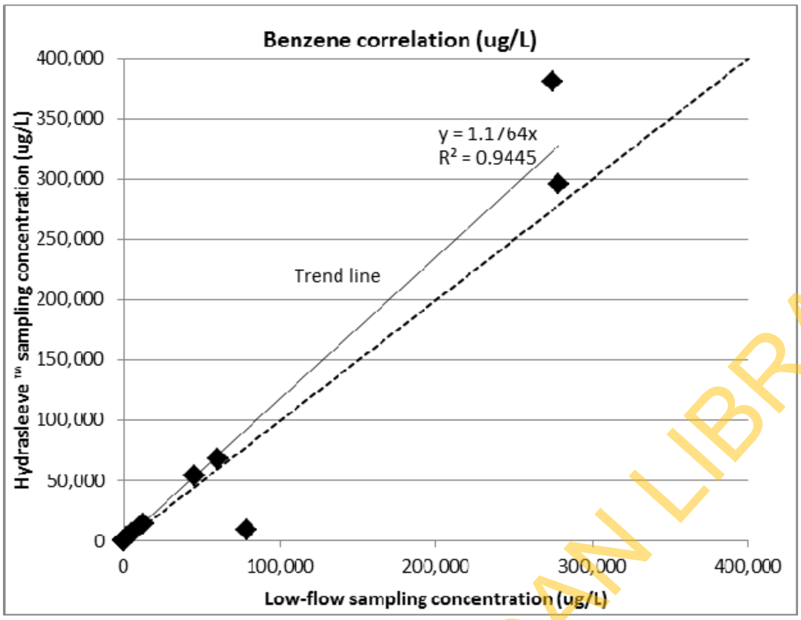

Figure 1. Combined data for benzene showing low-flow is a good predictor of low-flow results

Contaminant Stratification

Two of the three wells selected for shallow and deep sampling showed good correlation between the results. Overall, shallow results were in the same order of magnitude as respective comparative deep samples and no contaminant stratification was evident in water columns.

DISCUSSION AND CONCLUSION

No-flow results consistently produced good predictions of the low-flow results across an extensive analytical suite and range of concentrations. At one site the move to no-flow has successfully been endorsed by the EPA accredited Auditor.

No contaminant stratification was evident. However, this does not confirm whether there is no stratification present, only that further investigation into the effectiveness of no-flow samplers in series versus other stratification tools should be considered.

The commercial benefits of no-flow sampling are based predominantly on the reduced time required to collect grab samples in comparison to purging. However, the benefits are limited for the extensive suite which requires 2 L sample volumes and as a result the extended time spent transferring sample from no-flow sampler to analysis bottles. Additionally the manufacturer recommends 3 days for stabilisation on installation of the 2 L sampler.

Based on this there is a 28% commercial benefit in using 600 mL no-flow samplers over low-flow, while the use of 2 L no-flow samplers provides no commercial benefit to a client.

REFERENCES

Fernandes A.C. and Roberts P.G. (2001) Zero-purge groundwater sampling at a spent purifier media disposal site.

Environment Protection Authority Victoria (2000) A guide to the sampling and analysis of waters, wastewaters, soils and wastes. *Publication 441*

Environment Protection Authority Victoria (2000a) Groundwater sampling guidelines. *Publication 669*

RISK ASSESSMENT FOR LARGE FACILITIES OR PROGRAMS

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INTRODUCTION

Human health risk assessments (HHRAs) are used in decision making for many large facilities or environmental programs with numerous sites. Most state and federal risk assessment guidance documents were prepared with smaller, less complex sites in mind, so that application of typical methods addressed by these guidance documents is not always applicable, practical, or financially feasible. In addition, due to the number of sites within a facility, the time span of the risk assessment program can be long (many years), during which time there is the potential for staff turnover at the agency, regulated party, and the risk assessment firm, potentially resulting in inconsistencies in HHRA approaches and interpretation of results. Other approaches are needed for these large facilities and programs.

APPROACH

Over the past 5 years, CH2M has worked with many federal and commercial clients that have benefitted from the implementation of risk assessment programs on large facilities or environmental programs. These risk assessment programs have resulted in more efficient HHRA products and expedited agency review, while protecting human health and the environment. The types of approaches that have been successfully used over the past 5 years on various federal programs and large commercial facilities were reviewed and grouped into similar strategies for discussion.

RESULTS AND DISCUSSION

The large facilities and environmental programs reviewed had common components to their risk assessment programs, including a thorough and thoughtful risk assessment program planning stage with stakeholders. Various tools were generated during the planning stage, such as risk assessment protocol documents, standardized sets of exposure scenarios and assumptions for use at sites with similar characteristics, a list of interim deliverables, and standardized and streamlined reporting formats. The use of consistent risk assessment team members and senior reviewers was also a common aspect. These approaches helped ensure consistent work products and agency interpretation of results, streamline agency reviews, shorten project schedules, and reduce overall project costs.

CONCLUSIONS

Conducting numerous HHRAs at large facilities or within large environmental programs can become very complex, time-consuming, and expensive, and results may be used and interpreted in an inconsistent manner over time. However, if properly planned and executed, the use of risk assessment programs can be beneficial to both the regulated community and agencies. Successful risk assessment programs have common elements, including a thorough planning phase that documents processes and approaches, and endorsement by stakeholders. Consistent risk assessment team members and reviewers is also an important aspect contributing to efficiencies and quality.

DREDGING SYDNEY HARBOUR, ENVIRONMENTAL CONSIDERATIONS

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INTRODUCTION

Dredging projects are vital to maintaining the economic and logistical values of Australia's major ports and harbours. The historical use of Sydney Harbour has resulted in a wide range of environmental impacts, including contamination of underlying sediments. This contamination requires careful consideration when planning and conducting dredging activities.

The disturbance of contaminated sediments during dredging, with inadequate prior impact delineation, requires a robust monitoring regime and action plan to minimise the potential risk to human health and the environment. Monitoring regimes and action plans require flexibility to remain practical and efficient when adapting to the variability encountered during dredging projects.

METHODS

Tributyltin (TBT) was identified in sediments scheduled for dredging to deepen a shipping channel, allowing larger ship access to an iconic island location in Sydney Harbour. TBT was widely used as a biocide until it was banned from use in Australia as late as 2008. TBT is a persistent organic pollutant and has left a legacy of environmental impacts throughout Australia.

The lack of vertical and lateral delineation of TBT in the proposed dredging area at the subject site required a comprehensive Environmental Management Plan (EMP) to be developed and maintained throughout dredging activities.

Real time environmental monitoring; regular water quality sampling; and digital warning systems were major components of the EMP. Further challenges with generating spade-able material, bio-fouling of remote sensors, and treatment of TBT impacted supernatant were encountered during the program.

RESULTS AND DISCUSSION

An EMP for a site must be comprehensive and flexible to adapt to the many variables encountered during large scale dredging projects. The priority of scheduling regular field equipment maintenance and monitoring requires constant reinforcement with contractors. Regular communication with all stakeholders is vital to maintaining the importance of EMP compliance and utilising all available resources to develop innovative monitoring and process strategies. Accurate and robust environmental data collected during the project ensured minimal impact to the environment and human health.

COMPARISON OF IN-SITU SELF-SUSTAINING SMOULDERING COMBUSTION AND SEPR/S-ISCO METHODS FOR THE REMEDIATION OF COAL TAR DNAPL, BACCHUS MARSH, VICTORIA

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INTRODUCTION

A former manufactured gas plant (MGP) site in Bacchus Marsh, located approximately 50 kilometres west of Melbourne, Victoria, has been the subject of detailed multi-phase assessments of soil, soil vapour and groundwater. These assessments have identified soil and groundwater contamination, including the presence of coal tar in two discrete areas associated with former disposal wells. This has prompted studies of remediation feasibility and bench scale trials of selected technologies to remove the coal tar (DNAPL) components and ameliorate the associated residual soil and dissolved phase impacts. This paper focuses on the bench-scale trials conducted of two innovative in-situ approaches to the remediation of the coal tars – self-sustaining smouldering combustion (Self-sustaining Treatment for Active Remediation [STAR]); and surfactant-enhanced product recovery (SEPR)/surfactant-enhanced in-situ chemical oxidation(S-ISCO).

Bacchus Marsh is a regional centre consisting of residential and commercial land uses, surrounded by agricultural land. The region lies at the north western margin of the Port Phillip Basin, an area characterised by a Quaternary – Tertiary sedimentary sequence, underlain by basement rocks comprised of Ordovician metasediments and Devonian granite. The local Tertiary sediments consist of terrestrial and marginal marine strata that are coal bearing, with the prominent Maddingley Coal Seam commercially exploited approximately 4 km south of the site.

The local geology/hydrostratigraphy consists of a Quaternary age sequence of silts and clays coarsening downwards into basal gravels (the Shallow Alluvial Aquifer), underlain by interbedded lignite (associated with the regional coal-bearing strata) and clay (a local aquitard), which is in turn underlain by clayey sands interpreted to correspond to the Merrimu Gravel Member of the Werribee Formation (the Merrimu Aquifer). The coal tars have migrated to the base of the Shallow Alluvial Aquifer, which has associated dissolved phase impacts; the Merrimu Aquifer is not impacted.

METHODS

A detailed remediation feasibility study identified two preferred candidate technologies for the remediation of coal tar DNAPL at the site:

(a) STAR; and
(b) SEPR/S-ISCO

Bench scale treatability studies of the preferred technologies were conducted in two phases, as shown in Table 1. The methodologies utilised in each are summarised in the following sections.

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STAR

Column testing was conducted using an insulated steel reaction vessel containing a 12 cm thick sample of the test media – homogenised tar-impacted site soil and site lignite in phases 1 and 2, respectively. Testing used a base set of conditions comprising ignition temperatures of 300 - 400ºC and an air flux of 3.0 - 9.0 cm/s, with the test conditions modified as necessary to identify suitable conditions for self-sustaining smouldering.

Where self sustaining smouldering was observed, average peak temperature and smouldering front propagation velocity was derived by the analysis of data from thermocouples placed at 2 cm intervals throughout the column.

Table 1. Treatability Phases and Objectives of Bench Testing

Phase	STAR	SEPR	S-ISCO
1	Ignition/smouldering characteristics & off gas emissions	Surfactant selection and dosage	Surfactant selection and dosage
2	Lignite smouldering potential	Independent surfactant assessment	Independent surfactant assessment Oxidant selection and dosage

SEPR/S-ISCO

In Phase 1, bench scale laboratory treatability studies were conducted to assess the effectiveness of seven proprietary surfactant and co-solvent blends (EthicalChem). For the SEPR process, the screening tests were conducted on NAPL samples with the S-ISCO screening tests performed on homogenised (impacted) site soil. Surfactant selection for SEPR was based on the ability to desorb and solubilise the DNAPL (allowing migration to recovery wells) and for S-ISCO the ability to form a stable emulsion facilitating improved oxidant exposure over a longer period. Dosage tests were then conducted on the optimal SEPR and S-ISCO surfactants to evaluate the most practical and effective dosage rates for each process.

Phase 2 included baseline characterisation and Matrix Oxidant Demand (MOD) testing prior to comparative bench trials. The comparative trials evaluated matrix- and base-activated persulphate and S-ISCO. S-ISCO was evaluated using the preferred SEPR/S-ISCO surfactants using both persulphate and peroxide. Five ISCO formulations were evaluated.

RESULTS AND CONCLUSIONS

The results of the treatability trials to date indicate that both STAR and SEPR/S-ISCO could be applied at the Site.

Cores of impacted source material treated using STAR showed a 99.2% decrease in the total organic contaminant mass. No volatile compounds and only trace SVOCs were present after treatment. The lignite, which immediately underlies the source zone, was observed to be readily combustible. This is considered to be a significant constraint and will require risk mitigation measures to avoid unintended combustion of materials outside of the target treatment zone (e.g. sheet piling), in the event of pilot or full scale site application.

Based on the testing of site-derived source material, EthicalChem's surfactant blends MX-7 (SEPR phase) and VeruSOL-3 (S-ISCO phase) at dosages of 25 g/L were identified as the optimal surfactants for a SEPR/S-ISCO program. Criteria for surfactant selection for SEPR included high coal tar mobility after mixing and high propensity for settling out of solution. The criterion for surfactant selection for the S-ISCO phase was high solubilisation of the coal tar, to optimise oxidant contact and contaminant destruction in the aqueous phase. Oxidant demands and comparative oxidant treatment of the coal tar will be used to make a final determination of the remedial strategy with a view to undertaking a pilot trial during 2015.

DIRECT INJECTION OF EMULSIFIED VEGETABLE OIL FOR CHLORINATED SOLVENT REMEDIATION

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INTRODUCTION

Since 2012 a full-scale enhanced *in-situ* bioremediation (EISB) groundwater treatment system has been operational at a commercial site in Sydney. The remediation site covers an area of approximately 4.0 hectares and consists of the source site and affected neighbouring properties. The contaminants of significant concern at the site included tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (DCE) and vinyl chloride (VC). To date EISB has been successful in reducing the mass of chlorinated solvents in groundwater and has significantly reduced the areal extent requiring remediation. Hydrogeological modelling software has been used to estimate that approximately 5114 kg of combined PCE, TCE, DCE and VC have been removed from the subsurface since 2007, representing a 92% decrease.

To target the remaining dense non-aqueous phase liquid (DNAPL) source zones at the Site and further enhance the remediation performance, changes were made to the EISB system including the electron donor and method of injection. The original EISB system continually recirculated groundwater through extraction and injection wells and amended the groundwater with sodium lactate, a rapidly fermenting electron donor to enhance the native bacteria capable of breaking down PCE. This system has been modified to a direct injection strategy using emulsified vegetable oil (EVO) as the electron donor.

EVO was selected as it is a cost effective, slow release electron donor with greater hydrogen release efficiency. Because EVO undergoes slow fermentation it maintains a sustained release of electron donor which enables a once off direct injection targeting the individual Source Zones. Emulsification of the vegetable oil ensures small, uniform droplet sizes that distribute evenly throughout the source area.

AECOM was the principal contractor for transitioning from a groundwater treatment system to direct injection of EVO into existing source areas. The injection strategy was designed by Geosyntec Consultants, the remediation injection wells were installed by Terratest and Numac Drilling and Enviropacific was the civil engineering subcontractor.

METHODS

Injection Targets

A target injection concentration of 0.5 to 1.5% EVO solution was required within the aquifer dependent on treatment area. To ensure adequate overlap during injections a radius of influence of 4 m from each well was applied with an effective porosity for the aquifer assumed to be 0.20. Based on effective pore volume, in order to reach saturation 10,048 L was required per metre of screened interval. Overall 19,550 litres of EVO was needed with a total fluid volume of 1,200,000 litres proposed to be injected across the target areas.

Installation

The site was separated into five target injection areas and included both source and dissolved phase zones. New and existing wells were utilised for targeted injections of EVO. On this basis, a total of 42 locations were utilised during injections consisting of 29 existing wells retrofitted to accept injection equipment, 7 new vertical injection wells, 2 new injections wells inclined at a 25^{o} angle and 4 temporary direct push point wells.

Batching and Delivery

A portable batching system designed and operated by Enviropacific for mixing concentrated EVO (at 60%) with potable water and vitamin B12 (for bacteria optimisation) was used to achieve concentrations of 0.5 to 1.5% based on the area of injection. PVC delivery lines from the batching system to the five target injection areas were installed allowing batching and adjustment to occur at a central location during operation. A portable manifold system was constructed allowing simultaneous injection into wells within the targeted area as well as precise control of flow rate and pressure. Injection was carried out during 8 to 10 hour shifts, 5 days a week. The order of injection into the five injection areas was considered. Injection starting at the most down gradient injection area in the dissolved phase zone and worked back towards the injection area in the source zone.

RESULTS AND DISCUSSION

Between February and April 2015, a total of 1,093,015 litres of EVO solution was injected into the aquifer. A summary of the injection volumes is provided below.

Table 1. EVO Injection Summary

	Injection Duration (days)	Volume of EVO solution (L)	Concentration of EVO Solution (%)
Area 1	9	170,360	0.5
Area 2	9	112,905	0.5
Area 3	9	229,330	1.0
Area 4	7	170,190	0.5
Area 5	13	410,230	1.5
TOTAL	47	1,093,015	-

Baseline groundwater sampling was conducted prior to the EVO injection works with samples being analysed for Volatile Halogenated Compounds (VHCs), Total Organic Carbon (TOC), chloride and microbial assays. Performance monitoring sampling will be conducted on a monthly basis to track the continual mass removal of contaminants and the aquifers response to the EVO.

Figure 1:EVO batching system

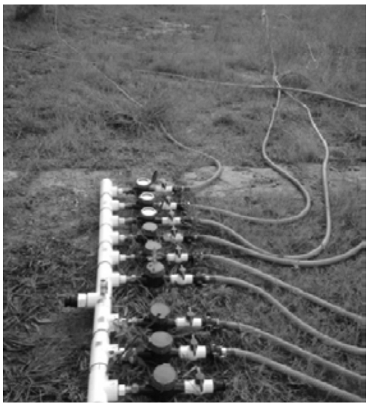

Figure 2: EVO injection manifold

CONCLUSION

AECOM's full scale EISB system has been successful in remediating the dissolved phase chlorinated solvent plume at the Site. Between February and April 2015, approximately 1.1 ML of EVO solution was injected into the aquifer to target the remaining DNAPL source areas. Performance monitoring sampling will be completed monthly to monitor the aquifer conditions and determine if repeat injections are required in select areas of the Site.

MULWALA EXPLOSIVES AND CHEMICAL MANUFACTURING FACILITY — AN INTEGRATED APPROACH TO GROUNDWATER MANAGEMENT

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INTRODUCTION

The Mulwala Explosives and Chemicals Manufacturing Facility was commissioned in 1943. The site produces raw materials, propellants and high explosive compounds for arms and artillery ammunition. Soil and groundwater contamination associated with historical site operations has been subject to numerous investigations over the past 20 years. These investigations delineated groundwater plumes with elevated levels of nitrate (>50 mg/L) and sulphate (>250 mg/L) extending off-site. In 2007, a four phased Remediation Implementation Plan was developed to address the identified groundwater impact and AECOM has been commissioned through the Department of Defence Environmental Remediation Program to undertake various work elements associated with the Remediation Implementation Plan.

METHODS

The principal intention of the management and remediation strategy provided in the Remediation Implementation Plan is to mitigate the mass of contaminants that may be contributing to on-going off-site groundwater impact by addressing contaminant source zones.

The Remediation Implementation Plan outlines a number of integrated work elements including completion of a hydraulic containment trial (HCT); installation of a full scale hydraulic containment system (HCS); source zone capping; and soil and groundwater remediation activities.

Following the completion of the HCT and source zone capping, AECOM undertook a hydraulic containment optimisation study. The objective of the study was to review the practicalities of installing a full scale HCS and involved a data gap review and collection of additional data; a feasibility study of extracted groundwater management options; a groundwater licensing appraisal; groundwater modelling (including an assessment of groundwater flow conditions, well placement and capture zones); and preliminary HCS infrastructure design.

Groundwater modelling has been undertaken to estimate a daily groundwater extraction volume that would be required to meet the objective of hydraulic containment (i.e. mitigate the off-site migration of impacted groundwater). Due to the complex issues associated with the management of the off-site migration of impacted groundwater, project stakeholders have advanced the project in the short term by the implementation of hydraulic containment in a portion of the aquifer located down hydraulic gradient of the most significant contaminant source zone. This provides the opportunity to operate a HCS on a manageable scale and assess whether modelled groundwater extraction estimates can be practicably applied and managed. Further, this will enable an assessment as to whether a contaminant source capture approach (as opposed to a broader hydraulic containment approach) will have a beneficial effect on groundwater quality over the greater investigation area.

Whilst the HCS is intended to mitigate the off-site migration of impacted groundwater from the most significant source zone, nitrate contamination currently residing within soils in this area is considered to be a primary on-going source of groundwater impact. As this area remains *in situ*, consideration of potential remediation options of this source zone is also required.

RESULTS AND DISCUSSION

Based on the outcomes of the hydraulic containment optimisation study, additional groundwater extraction wells have been installed to compliment the extraction network installed as part of the HCT. A number of scenarios have been simulated via groundwater modelling to inform extraction requirements. The scenarios chosen were based on providing an understanding of the total extraction rate likely to be required and which wells are likely to be most effective to achieve capture of groundwater migrating from the targeted source zone.

Following commissioning of the HCS, the HCS will require a program of ongoing operation and maintenance to monitor groundwater capture and assess the efficacy of the HCS in mitigating the off-site migration of impacted groundwater. The groundwater pumping configuration of the HCS is likely to require optimisation to achieve efficient plume interception and also to respond to seasonal / climatic changes.

CONCLUSIONS

A series of steps have been established which are required to achieve the overall project objective, that is, the restoration of groundwater beneficial uses off-site. These steps will be revisited and may be refined during successive phases of the Remediation Implementation Plan as the Conceptual Site Model is further developed and additional groundwater management and remediation actions are completed.

The presence of sensitive infrastructure in proximity to source zones presents a key challenge to the remediation of the contaminant mass. It is noted that the reduction of the contaminant mass residing within the targeted source zone is likely to reduce the operational timeframe of the HCS. As such, in conjunction with groundwater management via hydraulic containment, remediation options of the contaminant mass in source zones is also being progressively assessed.

As the Remediation Implementation Plan was developed in 2007, it has been considered appropriate to revisit previously proposed remediation technologies to assess the relevance of these technologies based on additional data obtained since 2007, and to assess constraints presented by current site conditions (i.e. sensitive infrastructure).

REFERENCES

AECOM (2014) *Initial Phase 2 – Hydraulic Containment System Optimisation Report, Thales Australia Limited, Bayly Street, Mulwala*

HLA (2007) *Further Investigations and Source Zone Practicability Review, Thales Australia, Mulwala, NSW*

DATA QUALITY SESSION FOR CLEAN-UP 2015

Data quality – in particular reliability and comparability – is a matter of importance to end-users of laboratory data such as environmental regulators, consultants and site owners/managers, who have to make decisions based on that data. An example of a key concern might be the degree of comparability between analysis results from different laboratories, each with potentially different analysis or extraction methods and sample handling protocols, or for samples collected using different field sampling methods.

Analytical laboratories typically ensure data quality through a range of mechanisms, such as NATA Accreditation, and matrix Certified Reference Materials and proficiency testing from accredited providers such NMI Australia. Matrix CRMs are important as quality control tools for assuring the ongoing performance of test methods and the validity of associated test results, as well as a benchmark for comparing measurements made between different laboratories. Proficiency testing (PT) assesses the performance of different labs and analytical methods by comparing their results for a single sample; participation in proficiency tests helps provide end-user confidence in overall data quality and the reliability of results. NATA accreditation criteria include international standards ISO/IEC 17025 *General requirements for the competence of testing and calibration laboratories* and ISO/IEC 17020 *Requirements for the operation of various types of bodies performing inspection.* Through its third party, peer assessment process, at a scientific and technical level, it provides assurance of the facilities capability to produce reliable data. Whilst formally recognising a laboratory's competence, it requires the laboratory to have adequate quality assurance procedures, appropriate sampling practices, appropriately trained staff, etc. However, laboratory quality assurance is only one part of the big picture.

These two sessions will explore end-user views on data quality, considering current concerns and possible solutions. In the first session, representatives from each of four end-user groups will give their perspectives on the issue of data quality. The second session will be an open discussion, led by a panel comprising the four speakers:
- Site Owner/Manager: Mr Craig Barnes, Air Services Australia
- Regulator: Dr Erwin Benker, NSW EPA
- Auditor/Consultant: Dr Michael Dunbavan, Coffey
- Laboratory Analyst: Mr David Springer, ELIG president

Representatives of NATA and NMI Australia will also provide their perspectives on the value of good quality data in sound decision making in the environmental space.

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SINGLE PARTICLE ICP-MS (SP-ICP-MS) FOR THE DETECTION OF METAL-BASED NANOPARTICLES IN ENVIRONMENTAL MATRICES

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INTRODUCTION

During the last decade, the production and use of engineered nanomaterials (ENMs) have experienced a drastic increase, resulting in a potential risk of their release into the environment. Therefore, the study of their impact on the environment becomes crucial. The appropriate ecological risk assessment and management of ENMs in the environment requires quantitative measurements of both exposure and effects that should, ideally, be performed by in situ analysis and give physicochemical characterization. However, most analytical techniques (TEM, SEM, DLS…) are not suitable for environmental matrices since nanoparticle concentrations are very low.

Alternatively, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been found to be a promising technique for detecting and characterizing metal nanoparticles at very low concentrations. SP-ICP-MS is fast and efficient and can provide more information than other currently available techniques. It can lead to the determination of particle size, size distribution, particle number concentration, and the concentration of dissolved metal. Moreover, it can distinguish between particles of different elements.

The aim of this work is to investigate the efficiency of SP-ICP-MS for the detection and characterization of metal nanoparticles in environmental matrices where they can be involved in various physicochemical processes as shown in Figure 1.

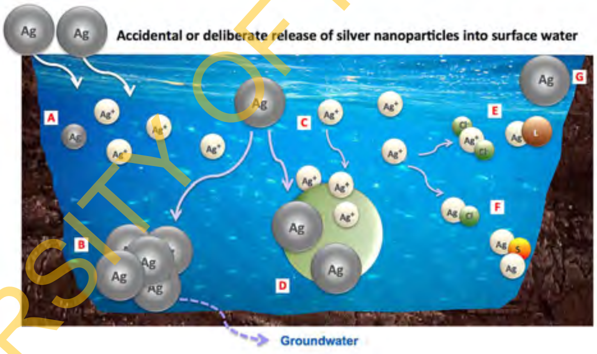

Figure 1 Possible fates of silver nanoparticles in surface waters: (A) Dissolution process leading to free ions release and smaller particles; (B) Aggregation into larger particles, which may settle out of the water, depending on the aggregate size; (C, D) Adsorption of released Ag+ and nAg, respectively, onto other solids present in the water; (E) Formation of soluble complexes; (F) Reaction with other components in the water, which may result in precipitation; (G) nAg remaining stable.

METHODS

A PerkinElmer NexION® 350X Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for data acquisition using the Nano Application Module within Syngistix™ for ICP-MS software. Commercially available suspensions of gold and silver nanoparticles were used in this work. A NIST reference material (RM 8013) consisting of a suspension of gold nanoparticles (60 nm nominal diameter, 50 mg/L total mass concentration and stabilized in a citrate buffer) was used to determine the nebulization efficiency. Suspensions of silver nanoparticles were purchased from Ted Pella Inc.: citrate coated (40 and 80 nm nominal diameter) and bare (80 nm nominal diameter) nanosilver suspensions (product numbers. 84050-40, 84050-80 and 15710-20SC, respectively).

RESULTS AND DISCUSSION

Figures 2&3 show the evolution of the average particle diameter and the percentage of dissolved metal over time in both pure and river water. In all cases, the average particle size of the persistent nanoparticles remains substantially constant (Figures 2a, 3a). For suspensions of particles with a nominal diameter greater than 40 nm, between 50 and 80% of the particles persist for at least five days of equilibration in pure and surface water (Figures 2b and 3b).

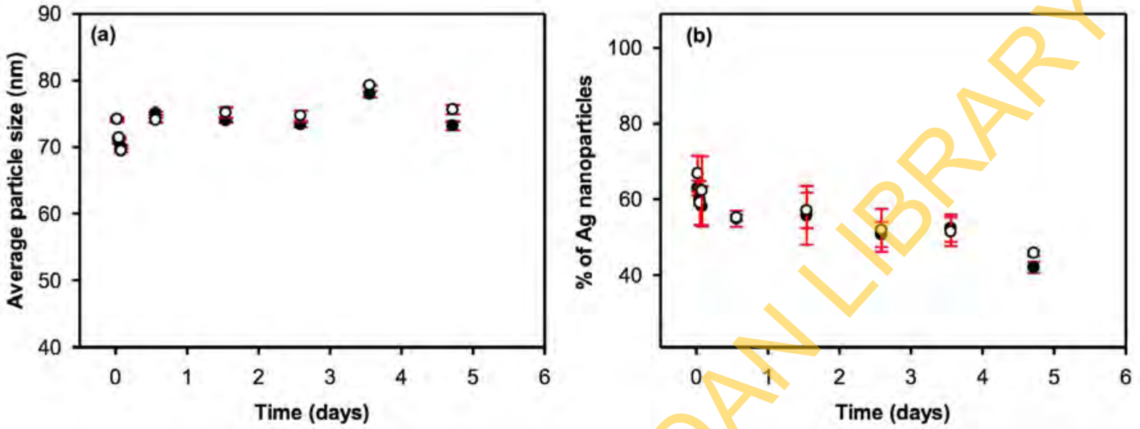

Figure 2 **Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (l) and surface (o) waters. Waters were spiked with 80 nm citrate-coated nAg, and the total metal concentrations were equal to 72.2 and 72.4 ng L^{-1} in DI water and surface water, respectively**

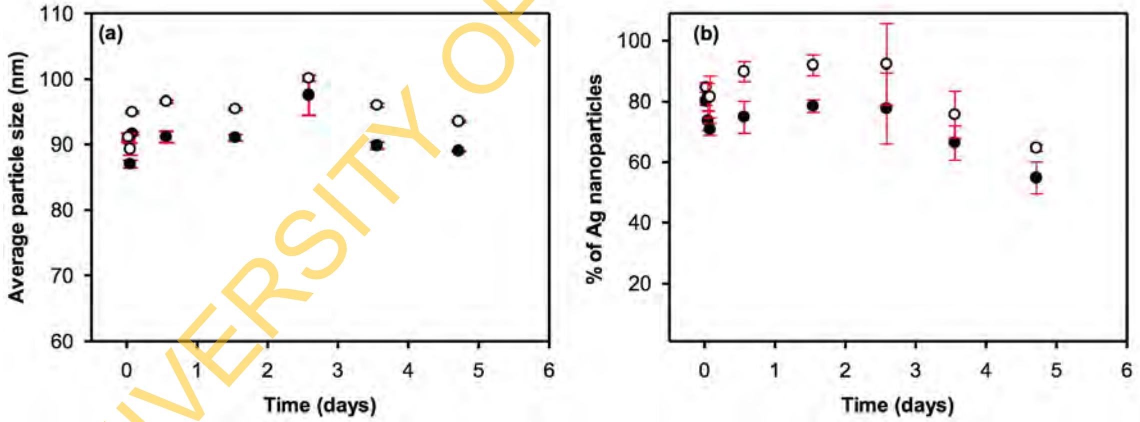

Figure 3. **Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (l) and surface (o) waters. Waters were spiked with uncoated 80 nm nAg, and the total metal concentrations were equal to 196.4 and 200.8 ng L^{-1} in DI water and surface water, respectively.**

CONCLUSIONS

SP-ICP-MS is practically the only suitable technique that can provide such information on the fate of metal nanoparticles at very low concentrations in environmental waters. Although this study only showed the effectiveness of the technique in the particular case of nAg in river water, it is, without any doubt, applicable to other types of metal and metal oxide nanoparticles in a variety of complex matrices form wastewater, surface water, effluents.

DETERMINATION OF TOTAL RECOVERABLE HYDROCARBONS (TRH) IN SOIL USING SOXHLET EXTRACTION AND GC-FID

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INTRODUCTION

Petroleum hydrocarbons are regarded as a major environmental contamination problem worldwide. High levels of variability in methods used to extract petroleum hydrocarbons and in the results obtained present a major constraint on industry's ability to comply with regulation and improve site remediation.

Recognising that methods are not specific for petroleum hydrocarbons and that results depend on the extraction conditions used, the 2013 amendment of the National Environment Protection (Assessment of Site Contamination) Measure (the 2013 "ASC NEPM") uses the term Total Recoverable Hydrocarbons (TRH) to describe the extracted biogenic and petrogenic hydrocarbons by selected solvents. It also specifies how to define and report new hydrocarbon fractions (>C10 – C16 (F2), >C16 – C34 (F3) and >C34 – C40 (F4) based on health screening levels (HSLs) adopted in the Canada-Wide Standard for Petroleum Hydrocarbons (PHC) in Soil. The ASC NEPM allows the use of performance-based analytical methodology for TRH in soil. Laboratories are able to select from a range of extraction and analysis techniques, provided these can be demonstrated to be equivalent to an agreed reference method and their ongoing performance meets an acceptance criterion based on a suitable reference material.

The reference method detailed in this document is based on the reference method developed for the Canadian Council of the Ministers of the Environment (CCME Tier 1 method) and adapted to meet NEPM requirements for calibration and reporting of fractions. Results obtained using the reference method and alternate extraction techniques have been compared in a NEPM variant study.

METHOD

Extraction and Analysis

Soil samples were extracted with n- hexane:acetone (1:1 v/v) in a Soxhlet apparatus for at least 16 hours, the extracts were solvent-exchanged to n-hexane: dichloromethane (1:1 v/v) and then activated silica (100°C, min 24h, 3 g into 5 g sample) was used to remove any polar compounds. The solvent was exchanged to toluene and analysed by GC-FID. The analysis was performed on an Agilent 7890 GC-FID equipped with a multimode inlet operated in splitless mode. Hydrogen was used as the carrier gas. Injection volume was 1 µl.

Calibration

Calibration against external standards of mixed hydrocarbons was performed as specified in Schedule B3 of the 2013 ASC NEPM by calculating response factors for representative hydrocarbons from each fractions (C14 for F2, C24 for F3 and C34 for F4) and integrating fractions in the sample between the retention times corresponding to the ends of the marker peaks (C10, C16, C34 and C40). TRH values (>C10 – C40) were obtained by summing results for F2 – F4. Calibration solutions were prepared using Certified Reference Materials (CRMs) NIST 1494 (C10 - C34 hydrocarbons) and Restek Florida TRPH (C36).

RESULTS, APLICATION AND DISCUSSION

Inlet Optimisation

Optimisation of inlet performance was done to meet mandatory criteria for instrument performance specified in the CCME Tier 1 method: the response factors for nC40 must be within 30% of the average of the nC10, nC16 and nC34 response factors and the response factors for the alkanes nC10, nC16 and nC34 must also be within 10% of each other. The use of a multimode inlet with a drilled Uniliner® made a significant improvement over standard split-splitless injection technique.

Table 1. Calculated RFs to monitor multimode inlet performance and peak discrimination for drilled Uniliner®

Bracket	RF-F2 (C14)	RF-F3 (C24)	RF-F4 (C36)	RF C40	Relative difference of C40 response
1	15.5	15.4	16.5	14.8	6%
2	15.8	15.8	16.8	15.7	2%
3	16.3	16.3	17.3	16.3	2%
4	17.6	17.7	18.0	17.0	4%
5	16.2	16.3	17.7	16.7	0%

Application: Certification of Reference Material and Comparison of NEPM Method Variants

The method was used to assign reference values for a new CRM NMIA MX015 that can be employed to assist Australian laboratories in demonstrating TRH method performance. NMIA MX015 is a hydrocarbon-contaminated refinery waste soil diluted with river sand. It has recently been used in an Australian proficiency study.

Schedule B3 of the NEPM (2013) recommends four sample extraction methods: soxhlet, sonication, tumbling with acetone:dichloromethane 1:1 v/v and accelerated solvent extraction. All four method variants were used to analyse a common set of CRMs sourced from RTC/ Sigma Aldrich (CRM372, CRM355 and CRM350), BAM (ERM-CC017 and spiking K010 mixture), NMI (NMIA MX-015) as well as spiked clay samples. The data was used to assess and compare the performance of these extraction techniques against that of the reference method.

Table 2. Comparison of NEPM extraction methods with NMI reference method

Matrix	Extraction efficiency normalised to soxhlet method, %recovery		
	Tumbling	Sonication	ASE
CRM372	78	92	84
CRM355	89	99	93
CRM350	99	83	90
ERM-CC017	91	90	102
MX015	93	80	110
K10 Spiked clay	90	80	114

CONCLUSIONS

The NMI Reference method links the NEPM methodology with the HSLs derived from the CCME Tier 1 method. The method variants studied yield 80-120% recovery compared to the benchmark soxhlet method for the materials studied. A new CRM has been developed and its suitability assessed in a proficiency study

REFERENCES

National Environment Protection (Assessment of Site Contamination) Measure (NEPM) (1999) (April 2013), NEPC 2013, Canberra.

Canadian Council of Ministers of the Environment (CCME) (2001), Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method.

TOTAL RECOVERABLE HYDROCARBONS IN WATERS: A CHEMIST’S PERSPECTIVE ON THE ANALYSIS OF SEMIVOLATILE PETROLEUM HYDROCARBONS

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INTRODUCTION

The examination of groundwater is an integral part of most contaminated site investigations and subsequent remediation. Despite this, the contaminated site NEPM (1999 amended 2013) Schedule B3 provides no specific guidance on methods for the examination of groundwaters.

Most Australian laboratories will examine waters for semivolatile total recoverable hydrocarbons using dichloromethane extractions based on US EPA method 3510C. This method is a general purpose one designed for the isolation of a broad range of organic compounds from waters. Where this method is used primarily on groundwaters from sites contaminated with petroleum, the non-specific nature of the extraction can lead to the reporting of false positives which are assumed to be petroleum hydrocarbons..

A conventional understanding of TRH analysis is that subjecting an extract to silica gel clean up will remove naturally occurring organic matter and that subsequent analysis of the extract will reflect petroleum hydrocarbons present in the samples.

This study demonstrates how different samples respond to different solvent extractions and to silica gel clean up and provides some insight into potential pitfalls of assuming total recoverable hydrocarbons equate with petroleum hydrocarbons, in particular following silica gel clean up.

METHODS

Samples

A series of samples were screened for the presence of material that produced a response by gas chromatography with flame ionisation detector in the semivolatile range of TRH - >C10 to C40. Candidate samples selected included samples from:

- A site contaminated with LNAPL (aqueous dissolved only).
- Leachate from a landfill containing putrescible material
- Surface water contaminated with oils from decaying eucalyptus leaves
- Water from a contaminated industrial site containing phenolic compounds.
- TCLP leachate of soil rich in organic materials

Preservation

Bulk samples were subsampled into individual 100 mL bottles with each sample split and preserved by chilling or acidification to pH <2 and chilling.

Sample Preparation and Analysis

Samples were extracted in two ways:

1. Extraction using dichloromethane
2. Extraction using n-hexane

All extracts were subject to analysis for semivolatile TRH prior to and following silica gel cleanup.

Additional qualitative information was obtained by examining extracts using Gas Chromatography-Mass Spectrometry.

RESULTS AND DISCUSSION

Sample extractions demonstrate that dichloromethane is more likely to extract polar organic compounds than is hexane. This can be a source of false positives when the focus of the groundwater investigation is on petroleum hydrocarbons.

Examination of samples containing natural compounds such as eucalyptus oils show that silica gel clean up does not remove all components as the terpenoid compounds in eucalyptus oils cover a range of polarities.

Unweathered petroleum hydrocarbons have a high solubility in n-hexane and are easily extracted from waters. At the same time n-hexane is much less likely to extract organic acids and phenolics from waters and the chromatograms demonstrate that recoveries or extractable hydrocarbons form the landfill leachate and the contaminated industrial site are lower than for methylene chloride extracts. In some respects, the results of hexane extracts are closer to silica gel cleaned dichloromethane extracts and provide a potentially better indication of the presence of unweathered petroleum hydrocarbons.

CONCLUSIONS

Sample extraction, preservation and acid preservation influence the results for TRH fractions for different types of samples. Traditional dichloromethane semivolatile water extractions do not necessarily reflect the presence of petroleum hydrocarbons because the extraction was originally used as a technique for the extraction of semivolatile organic compounds, basic, neutral and acidic and not petroleum hydrocarbons in particular.

Where site investigations examining groundwater are particularly focussed on petroleum hydrocarbons, the use of more specific extractions (for example, a non-polar solvent for non-polar contaminants such as petroleum hydrocarbons) can yield provide a more accurate measure of the target contaminants.

Silica gel clean up may contribute to the removal of polar non-petroleum interferences but will not remove non-polar naturally occurring organic matter. In addition, it may also remove polar degradates of petroleum products.

When laboratory analysis yields unexpected or unusual data, contaminated site investigators may need to carefully consider the choice of analytical techniques, clean up and even instrumental analysis that the laboratory uses in order to obtain the best possible information about their particular site.

REFERENCES

National Environment Protection (Assessment of Site Contamination) Measure 1999, Schedule B3—Guideline on Laboratory Analysis of Potentially Contaminated Soils

US EPA (1996), Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, *SW-846*, United States Environment Protection Authority.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SPIKED AND AGED SOIL USING MODIFIED QuEChERS AND GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants that are ubiquitous in the environment and biota. PAHs are also one of the most extensively studied groups of organic contaminants due to their wide occurrence and potential impact on health. PAHs are by-products of the incomplete combustion of organic matter originating from anthropogenic (i.e. burning of fossil fuels) and natural sources (i.e. forest fires, volcanoes). Concentrations of PAHs are normally elevated in the environment within the vicinity of industrial land-use areas in comparison to residential or background sites. It is noteworthy that very high concentrations of PAHs in soil are reported from former gasworks sites (Thavamani et al. 2011). Contaminated soil at such sites may have concentration of PAHs above the health investigation level (HIL) and hence may require clean-up for specific land use including residential development. In this paper we evaluate PAH concentrations in soils spiked and aged for 18 months. These laboratory aged soils mimic field samples and we evaluate if residual concentration may relate to soil property and if it is above the HIL.

METHODS

Seven soil samples were collected from various locations in South Australia and Victoria, Australia and two of these soil types were spiked with selected PAHs (i.e. naphthalene, phenanthrene, pyrene and benzo[a]pyrene (B[a]P)) then aged for 18 months. The soil samples were analysed using a modified version of the Association of Analytical Chemists (AOAC) 2007.01 procedure (Anastassiades et al. 2003). In brief, soils were freeze dried and sieved to collect the <250 µm fraction before further processing. Approximately 0.1 g of spiked sample is extracted using a mixture of acetone / hexane (1:1 v/v, 2 mL). Then 0.1 g of the AOAC 2007.01 extraction salt (containing magnesium sulfate and sodium acetate) is introduced and the contents are vortexed for 5 min for further extraction. This is followed by centrifuging the extract for 5 min at 2943 g Then 1 mL of the supernatant is transferred to the dispersive solid phase extraction (d-SPE) tube and cleaned up by vortexting the contents for 5 min, followed by centrifuging at 13,450 g for 5 min. The clean extract is ready for analysis of PAHs by Gas Chromatography Mass Spectrometer (GCMS). A 30 m x 0.25 mm ID and 0.25 µm DB-5MS column was used with helium as carrier gas (flow rate = 1.2 mL/min). Injector temperature is maintained at 270^{0}C while the oven temperature was programmed with an initial temperature of 60^{0}C, ramped to 210^{0}C at 12^{0}C/min then 8^{0}C/min to 340^{0}C with 5 min hold time. Laboratory blanks and a reference material (European Commission BCR® - 524 - industrial soil) were included and recoveries of internal and surrogate standards were used as a measure of QAQC.

RESULTS AND DISCUSSION

All spiked PAH compounds analysed in these soils were found to be present in the <250 µm soil fraction (Table 1). The concentrations of pyrene and B[a]P for reference material were within the certified values (i.e pyrene was 176 mg kg^{-1} and certified value was 173 mg kg^{-1} (RSD = 1.3%) and for B[a]P was 6.7 mg kg^{-1} and certified value was 8.6 mg kg^{-1} (RSD = 17.7 %). The recoveries of deuterated PAHs were in a range of 80 – 110%.

Table 1. Concentrations (mg kg^{-1}) of PAHs in spiked soils found after 18 months of aging

Soil I.D.	NAP	PHE (mg/kg)	PYR	B[a]P
KBA Σ1550	1.1	3	105	30.3
KBA Σ2790	2	8.1	89.6	56.9
KBA PHE 750	-	30.4	-	-
KBA PYR 1500	-	-	428.7	-
KBA BP 200	-	-	-	146.9
KBA BP 150	-	-	-	148.2
DUA BP 150	-	-	-	50
DUA BP 200				150
DUA Σ1550	1.6	7.7	105	39.4
DUA NAP 2000	10.6	-	-	-
DUA NAP 1500	3.2	-	-	-

NAP –naphthalene; PHE – phenanthrene; PYR-pyrene; B[a]P- benzo[a]pyrene
KBA – Kersbrook, South Australia; DUA – Dublin, South Australia.

It is noteworthy that concentrations of low molecular weight and more volatile PAHs (i.e. naphthalene) determined in spiked and aged soil samples are much lower in comparison to the initial concentrations at which these soils were spiked (Table 1). This was also the case for phenanthrene and pyrene spiked and aged soils and is indicative that these PAHs may be lost more easily. In contrast, both soil types that were spiked with B[a]P and aged for 18 months had concentration quite close to the spiked concentration. Significantly, a recent study on extractability of ^{14}C-B[a]P in aged soil has highlighted that there was limited loss of ^{14}C-B[a]P by degradation in four contrasting soil types (Duan et al. 2015). Additionally, the bioavailability of B[a]P in different spiked and aged soils using a juvenile swine model ranged from 22 to 63 % (Duan et al. 2014).

CONCLUSIONS

Overall significant losses were observed for the lighter PAH in two soil types that were spiked and aged for 18 months. In comparison B[a]P was still present close to the concentration at which the soils were spiked before aging. The bioaccessibility of these PAHs in aged soils is being investigated.

REFERENCES

Anastassiades, M., Lehotay, S.J., Stajnbaher, D., Schenck, F.J. (2003) Fast and easy multiresidue method employing acetonitrile extraction / partitioning and “dispersive soild-phase extraction” for the determination of pesticide residues in produce. *J. AOAC INT*. 86 (22): 412-431.

Duan, L., Palanisami, T., Liu, Y., Dong, Z., Mallavarapu, M., Kuchel, T., et al. (2014) Effects of ageing and soil properties on the oral bioavailability of benzo[a]pyrene using a swine model. *Environ Int.* 70: 192–202.

Duan, L., Naidu, R., Liu, Y., Palanisami, T., Dong, Z., Mallavarapu, M., Semple, K. T. (2015) Effect of ageing on benzo[a]pyrene extractability in contrasting soils, *J. Hazard Mater*. http://dx.doi.org/10.1016/j.jhazmat.2015.04.050

Thavamani, P., Megharaj. M., Krishnamurti, G. S., McFarland, R., Naidu, R. (2011) Finger printing of mixed contaminants from former manufactured gas plants (MGF) site soils: Implications to bioremediation. *Environ Int.* 37 (1):184-189.

THE ROLE OF MEASUREMENT AND QUALITY ASSURANCE IN SUPPORTING ENVIRONMENTAL POLICY AND REGULATION FOR CONTAMINATION MANAGEMENT

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INTRODUCTION

Measurement is a vital part of environmental contamination management. Measurements are needed to generate the risk assessment data used by regulators to develop guidelines, as well as the data needed for the initial assessment of a site prior to remediation and the subsequent monitoring and evaluation phases. The use of appropriate methods and data quality is sometimes assumed, without due consideration of what is needed to ensure that these will be available.

This paper outlines several ways in which good measurement is integral to the effective implementation of policy within the environmental contamination area. Examples illustrating each of these are given, based on work done by the National Measurement Institute with the support of CRC CARE to facilitate the effectiveness of environmental policy.

ENABLING REGULATION AND END-USER RESPONSE

Good regulation sets boundaries that are based on sound data, for example, by choosing guideline or trigger values that have been demonstrated to be of toxicological significance. End-users may then be required to demonstrate their compliance with the boundaries set in regulation; this in turn involves acquisition of suitable data for scrutiny by regulators. In many cases, the guideline values used by regulators may have been developed from toxicological data based on measurements taken in a different jurisdiction, and application of those guideline values rests intrinsically on an assumption that the data will be comparable regardless of any differences in location, sample collector, laboratory, analysis method etc.

In practice, the full significance of health and environmental risks for many chemicals and other potential contaminants have often only been realised long after those substances have been developed and introduced into common use. Well-known examples of these include the liberal spraying of DDT and the use of radium to make watch hands fluorescent. Our ability to measure something often lags the discovery that it needs to be measured, and as a consequence measurement techniques are not always available at the level of accuracy required. Even after a need for improved measurement methods has been identified, it may take some time for suitable techniques to become widely available, as such techniques are often initially developed by laboratories for proprietary use. During this phase, there may be significant non-uniformities in the quality and reliability of data from different sources, which hinders their comparison or combination.

End-user compliance with regulation as regards management of specific individual contaminants is only possible if analytical methods of sufficient sensitivity in the appropriate environmental matrices are available. Suitable analysis methods are also required to generate the toxicological data upon which regulation is based. Ideally these methods should be complemented by suitable quality assurance (QA) tools such as reference materials and proficiency testing or interlaboratory comparisons.

Hexabromocyclododecane (HBCD) is a novel flame retardant used extensively as a replacement for polybrominated diphenyl ethers. The extent of global concerns regarding its impact on humans and the environment is demonstrated by its recent addition to the list of chemicals regulated under the Stockholm Convention for Persistent Organic Pollutants, an international treaty to which Australia is a signatory. HBCD is a key emerging contaminant for which both analytical capability and quality assurance tools are lacking in Australia, and CRC CARE has responded to this need by inviting the National Measurement Institute to develop an analytical method for quantification of HBCD in an environmental matrix.

ENSURING DATA RELIABILITY AND COMPARABILITY

The availability of measurement techniques on their own is not sufficient; QA tools such as reference materials and proficiency testing are also needed to ensure that data from different sources are comparable and reliable. For example, as noted above, the process of assessing measurements from a site against guideline values developed from toxicological data based on other measurements is effectively a comparison of data from very different sources, and one which often spans international jurisdictions. Data reliability and comparability is also a significant concern when data from multiple laboratories are involved.

Reference materials, particularly those with a certified value and associated uncertainty, provide laboratories with a useful means for calibration and standardisation of their analysis results. Reference materials generated from environmental matrices are especially helpful for laboratories working in this area.

Proficiency testing offers an objective assessment of comparability between measurements from different laboratories. Detailed feedback from PT providers can be also used by laboratories to assess the accuracy of their measurements, to evaluate the methods and instrumentation used, and to identify ways to optimise performance.

CRC CARE has recognised the value of QA tools to environmental policy implementation by supporting the NMI development of a certified reference material for Total Recoverable Hydrocarbon (TRH) in an environmental matrix and proficiency testing capabilities for perfluorooctane sulfonate (PFOS) and perfluoroocatanoic acid (PFOA). This is the first time either of these has been offered in Australia. TRH represents one of the world's most ubiquitous environmental contaminants, whilst PFOS/PFOA are major emerging contaminants known to be toxic to humans and wildlife, to accumulate along the food chain and to be highly resistant to degradation.

VERIFYING AND ENABLING POLICY ASSUMPTIONS

Implicit assumptions about measurement can also be found in policy, and there is often significant value in testing these. One such example can be found in Schedule B3 of the 2013 ASC NEPM, which specifies alternative standard methods for use by laboratories. The NEPM also allows for the use of other methods, provided the performance of these can be demonstrated to be equivalent to the standard methods, e.g. through the use of reference methods and materials. This implies, firstly, that the standard methods specified must be equivalent in performance or, at the least, the results produced using the methods are objectively and reproducibly comparable and, secondly, that appropriate reference methods and materials are available. Apart from developing suitable reference methods and materials, scientists can also contribute by conducting objective performance comparisons of the specified standard methods using common environmental materials. These can then be used to inform end-users of the degree of equivalence possible and the conditions under which that equivalence can be assumed, thus generating greater regulator confidence in data submitted for scrutiny.

In work supported by CRC CARE, NMI has undertaken an independent assessment of the four standard extraction methods specified by the NEPM for TRH analysis. The results of this assessment will facilitate adoption of the NEPM by assisting laboratories with evaluation of extraction techniques.

CONCLUSIONS

Good measurement enables effective environmental policy and regulation through the development of new or improved analysis techniques which are needed to provide data for policy development and to enable end-users to comply with guideline specifications; it also allows policy assumptions to be tested and verified. Furthermore, QA tools ensure the quality and reliability of data used by policymakers to allow better decision making.

PRODUCING TELEPHONE NUMBERS RATHER THAN REAL DATA FOR OUR MULTI-MILLION DOLLAR DECISION MAKING. A REVIEW OF DECISION CERTAINTY IN CONTAMINATED LAND ASSESSMENT AND REMEDIATION

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INTRODUCTION

"Doubt is an uncomfortable condition, but certainty is a ridiculous one!"
– Voltaire (1694-1778).

The convergence of **emerging contaminants** with their associated problems in their reliable low level detection, together with the development of conservatively derived assessment criteria have conspired to place a very heavy reliance on data of questionable certainty. This reliance is a significant concern as multi-million dollar decisions relating to site assessment and remediation, without any clear understanding of the uncertainty (which some would characterise as "error") which surrounds the data that is being used for these key decisions.

UNCERTAINTY – WHERE DOES IT LIE?

This paper clearly identifies the key areas of data uncertainty for both assessment and remediation/validation, especially for emerging contaminants, with focus on uncertainty in:

- Sampling;
- Analysis;
- Criteria Selection;
- Criteria Development;
- Scale-up for Site Characterisation;
- Decision Communication; and
- Risk Communication.

The additive and sometimes synergistic effects of these measurement uncertainties are discussed in a sequential manner, paralleling the various NEPM stages of data collection and interpretation, and decision making.

MANAGEMENT OF UNCERTAINTY – RULES OF ENGAGEMENT

This paper provides targeted recommendations to identify and hopefully reduce decision uncertainty, including the use of a simple "Management of Uncertainty in Decision Data (MUDD)" Checklist, designed to minimise the potential for costly and inappropriate decision-making. Recent examples will be provided using the emerging contaminants of ASBestos-IN-Soil (ASBINS) and PFCs (PFOA, PFOS, and certain FtS).

KEY REFERENCES

AnxietyBC (2009) "How to Tolerate Uncertainty" (http://www.anxietybc.com/sites/default/files/ToleratingUncertainty.pdf, accessed on 6 July 2015)

National Environment Protection (Assessment of Site Contamination) Measure 1999 (ASC NEPM), amended May 2013 (https://www.comlaw.gov.au/Details/F2013C00288, accessed on 6 July 2015).

CHALLENGES IN THE MEASUREMENT OF PFOS IN ENVIRONMENTAL SAMPLES: ARE THE NUMBERS MEANINGFUL TO ENVIRONMENTAL TOXICOLOGISTS AND REGULATORS

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INTRODUCTION

There have been long-standing differences between laboratories in the quantification of perfluorooctanesulfonate (PFOS). In many cases it has been difficult for a consultant to obtain consistency in results between primary and secondary laboratories. The big question for investigators and regulators is 'which result is correct?'

In an investigation of the authors' own laboratory performance in a proficiency study (AQA-15-03), the issue of PFOS analysis appears to be confirmed. An examination of PFOS results for an incurred residues and a spike on soil samples S1 and S2, suggested to the authors that laboratory results may be bi-modal (i.e. two separate data sets).

In a smaller study with five participant laboratories (Aquacheck PT round 460, February 2014) a spiking solution was supplied to participants for spiking into deionised water. In this study four laboratories clustered close to the spiked value and the fifth was a distinct outlier reporting almost twice the concentration of the material spiked. In this particular study, the analysis was effectively of a standard so, in all likelihood, removed other factors that could contribute to variation.

Standard methods for the determination of PFOS and other PFCs have from around 2009, onwards have all specified LCMSMS as analytical method of choice but distinct differences in the response of pure linear PFOS (available only as an analytical standard) in contrast to the technical mixtures found in product formulations and also available as certified analytical standards (see Naile et al, Voyksner and Meng, for example).

The extreme differences that on occasion occur between primary and secondary laboratories for PFOS analysis in particular may be, for the greater part, due to differences in calibration standards used by various laboratories. The author's sought to examine this by analysing soil and water samples containing incurred residues of PFOS and quantifying the data using two different analytical standards.

METHODS

91 samples from contaminated sites including two soils from the referenced proficiency trial were subject to analysis for PFOS by LCMSMS. The individual sample data was quantified using both a linear standard of PFOS and a mixed linear/branched standard (both certified standards source from Wellington Laboratories, Guelph, Ontario).

Statistical analysis of data was performed using Passing-Bablock bivariate regression (*MedCalc Statistical Software version 14.12.0 (MedCalc Software bvba, Ostend, Belgium; http://www.medcalc.org; 2014)*

RESULTS AND DISCUSSION

Regression analysis shows a clear-cut and significant difference in quantitative results depending on the choice of standard with distinctly higher results reported when using the pure linear PFOS standard for calibration.

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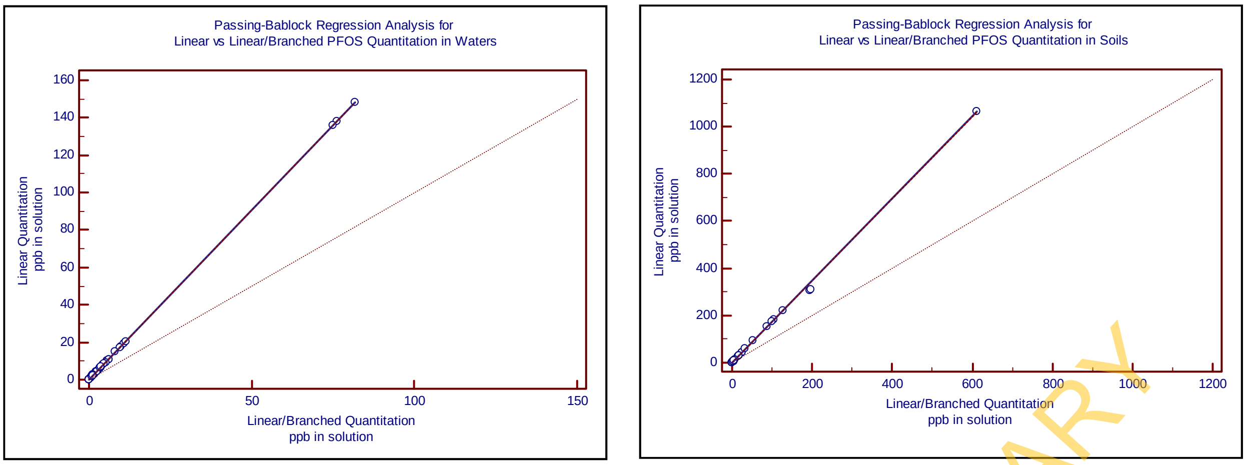

Figure 1. Bivariate regression analysis comparing quantitation using a mixed linear/branched PFOS vs. pure linear PFOS. The dotted line indicates equality between methods.

All the real world samples examined in the authors' laboratory show a distribution of linear and branched PFOS that corresponds to those found in source materials (AFFF used in fire fighting) and consistent with the historical manufacturing process for PFOS. Quantification using linear PFOS gives a result, on average 77% higher than that obtained with a mixed standard.

Whilst the differences in response between linear and branched PFOS species is well documented the impact on real world measurements has not been fully appreciated.

CONCLUSIONS

Where end users encounter significant differences between results from different laboratories, the use of different standards and the bias this introduces is the first issue that needs to be addressed by questioning which type of analytical standard is used by a particular laboratory.

The use of a single pure standard to quantify an aggregate of similar compounds is an established practice in analytical chemistry. For this to be valid the response (quantity of signal produced in the instrument per unit mass of target compound) must be the same across all peaks being quantified. Alternatively, the aggregate response of a mixed standard should be similar to the aggregate response of the mixture found in real world samples. In the case of PFOS, the pure linear standard quite clearly does not meet the brief.

Whilst the authors' own experience of real world samples suggest some variation in the distribution of isomers in environmental samples (many thousands of samples of soils and waters since gaining accreditation for testing in 2009), they believe that a mixed standard best reflects this reality. US EPA method 537 specifically calls for the use of a mixed linear branched standard.

From a regulatory perspective, an aggregate concentration for linear/branched PFOS provides a conservative number for risk analysis. On the other hand, a positive bias of 70 percent plus, is not useful particularly when comparing results to an established guideline.

The authors' own laboratory has been using a mixed linear/branched PFOS standard since commencing this testing and believe that this provides the most accurate number when analysing environmental samples.

REFERENCES

Naile, J. E., J. Seong Khim, J. N. House, P. D. Jones and J. P. Giesy. 2010. *Standard purity and response factors of perfluorinated compounds*, Toxicological and Environmental Chemistry, 92 (7), 1219 - 1232

Voyksner, R. D., C-K Meng. 2008. *Addressing the Challenges of Analyzing Trace Perfluoroocatanoic Acid (PFOA) and Perfluloroocane Sulfonate (PFOS) using LC/QQQ*, Application Note 5989-7790EN, Agilent Technologies, Inc.

Proficiency Study AQA 15-03. *PFOS/PFOA in Soil and Water*, June 2015, National Measurement Institute and CRC CARE

Aquacheck PT Scheme Report, *Round 460: Group: Major organic contaminants,* LGC Standards Proficiency Testing, Issue 1, 2014

US EPA Method 537, *Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)* Version 1.1, 2009

THE VALUE OF THE RIGHT RATHER THAN ACCURATE MEASUREMENT IN CHARACTERISING CONTAMINATED SITES

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INTRODUCTION

Characterisation of contaminated sites involves the collection and analysis of samples to inform understanding of the potential risks to human health and environment from contamination present on the site. Current policy and guidelines places much emphasis on evaluation of Data Quality Indicators (DQIs) and advocates use of NATA accredited methods by the laboratory.

In the quest for accurate measurement of small sub-samples collected from bulk media effort is focused on minimising concentration measurement uncertainty. This focus on DQIs often leads to simplifying assumptions as to what the concentration data can mean in the real world. Often these simplifying assumptions are not borne out in reality leading to cost and time overruns in remediation.

COMMON ISSUES IN SITE CHARACTERISATION

A key assumption in soil and groundwater analysis is that small subsamples are representative at the field scale. Soil is heterogeneous and small subsamples often do not represent heterogeneity in concentration variance within the soils. Similarly, groundwater hydrogeochemical conditions often change significantly between those in the aquifer and the surface, thus affecting solute speciation and solubility. Use of small samples for analysis may yield highly accurate analysis of contaminant concentrations, thus minimising the measurement error. However, little remains known about the prediction error when these concentration results are extrapolated to the field scale.

Therefore use of highly accurate concentration measurements provides only limited information on the overall decision error, which is largely dependent on the prediction error.

APPROACHES TO IMPROVE UNDERSTANDING OF PREDICTION ERROR IN SITE CHARACTERISATION AND ADJUSTMENT OF POLICY

The significance of prediction error is largely influenced by the assumptions on which most contaminated site characterisation assessments rely. For example, policy and guidance on sample locations and sample patterns are based on assumptions regarding shape and size of the contamination target, or on an assumption that the concentrations of contaminants measured in small subsamples are representative over a specific volume of soil.

Use of less accurate and less costly methods would allow for more intensive testing that could decrease the accuracy of the concentration measurement but also decrease prediction error by improving understanding of soil heterogeneity and contaminant distribution. For example, use of portable X-ray Fluorescent (XRF) spectroscopy allows for collection of significantly larger numbers of concentration measurements from the same sample on a repeated basis. While potentially not as precise as laboratory based analysis XRF can provide a significantly better characterisation of the soil heterogeneity at a much lower cost than an equivalent number of laboratory analyses. Figure 1 shows a comparison of concentration measurements from laboratory analysis of a single homogenised bulk sample and two particle fractions from that sample with those from XRF measurements collected for the same sample. The 5 XRF measurements on the sample show that Copper concentration varies considerable within the sample submitted for laboratory analysis. However, the single subsample analysed by the laboratory produced only a single copper concentration with no information on concentration variance. Concentration variance was more pronounced in the in the fine fraction, suggesting that the majority of the concentration heterogeneity is associated with the fine gain size of the soil. Analysis of the small proportion of coarse fraction shows lower and less variable copper concentrations than the fine fraction. XRF better defined the potential heterogeneity in soil than the single acid extract analysis.

An added advantage of the XRF analysis method is that concentration measurement is not destructive, thus allowing for repeat analysis of the exact sample tested.

Developing an understating of the soil heterogeneity on the sample scale is a critical aspect in understanding the reliability of any spatial distribution prediction made from the concentration measurements. The use of lower cost and higher intensity measurements could decrease the significance of prediction error in the characterisation of sites.

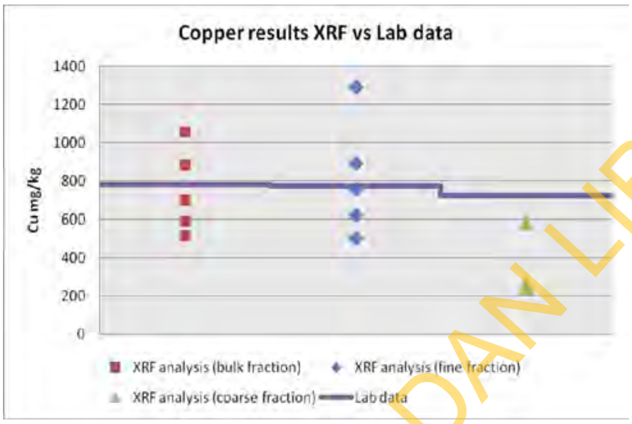

Fig. 1. Comparison of laboratory analytical results and XRF concentration measurements.

Another aspect is the choice of test methods used for laboratory analysis, which irrespective of NATA accreditation, may not be appropriate for all environmental conditions of the soil and groundwater. An example where existing NATA accredited method limitations occur is in groundwater sample analysis of hexavalent chromium concentration. The standard analysis is based on the colorimetric method and is widely used in groundwater testing. However, the limitations of the method such as limits on pH range and assumption that dissolved Fe is absent are often not adequately considered. This can lead to false positive measurements of hexavalent chromium. Use of infield co-precipitation method can overcome some of these limitations. Experiments have shown that at pH 5.2 in a solution only containing CrIII that the colorimetric method can give false positives for CrVI of around 12% of the total Cr concentration in solution while the co-precipitation method detected no CrVI. Experiments with solutions containing various concentration of FeII in solution also demonstrated that the co-precipitation method showed better recovery of the known Cr concentration in solution than the colorimetric method. While the method may not be NATA approved in Australia it could provide an alternative for analysis of hexavalent chromium concentrations in samples from environments where the colorimetric method would return false positive results.

CONCLUSIONS

Use of potentially less accurate lower cost field based methods may offer improved site characterisation outcomes and decrease prediction error in decision making. The lower cost methods allow for greater intensity of testing that better characterises the variance within and between samples. This allows improved characterisation and while not strictly in line with policy and guidelines result in lower risk of decision error. XRF methods can enhance characterisation of soil heterogeneity and delineation of impacts. Infield co-precipitation methods can provide more representative measurement of hexavalent chromium in some environments. Greater recognition of prediction error and alternative analysis methods in policy and guidance would encourage greater flexibility and clarity in improving site characterisation and decision making.

ENVIRONMENTAL MEASUREMENTS AS THE BASIS OF POLICY CHANGE — A CASE OF THE TAIL WAGGING THE DOG?

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INTRODUCTION

Environmental policy is based on the concept of protection of humans and ecosystems from impacts caused by anthropogenic inputs or changes. The scale of issues that policy instruments are designed to address ranges from local-scale impacts from finite volume releases of contaminants to planet-wide impacts from carbon emissions. For the purposes of this discussion we are focusing on the smaller end of the scale, where policy is set to protect humans from unacceptable risk based on exposure to contaminants in their environment. This is primarily accomplished through the setting of a maximum dose of a contaminant in different media (e.g., Maximum Contaminant Limits or MCLs for drinking water in the United States) that represent potential pathways for exposure. This approach has a number of limitations; the MCL may be limited by the Practical Quantification Level (PQL) of the substance in drinking water, policy lags behind science in understanding the risks presented by emerging contaminants, and policy lags behind science in the understanding of new pathways for exposure (such as risks from vapour intrusion). In each case measurements (new measurements or increased precision of existing measurements) are fundamental to refining, or to developing new policy (new measurements which identify new risks). What are the limitations to this approach and is there a better way?

Each of the above scenarios will be critically explored with a focus on how measurement has driven policy in the past and how it is likely to drive policy in the future. Possible new paradigms for proactive approaches will be explored, based on the lessons learned over the last several decades of environmental monitoring and risk-based policy development. Specific items to be considered include:

MCLs – Currently MDLs for TCE in water samples are in the range of 0.01 ug/L at commercial labs. In comparison, the advent of rigorous performance-enhancing drug testing in athletes has led to the lowering of MDLs for steroids to as low as 0.00025 ug/L (Deshmukh et al., 2011). MCLGs (Maximum Contaminant Limit Goals) are non-enforceable public health goals, which guide the setting of MCLs based on best available treatment technology and implementation cost. Discussion will focus on the future potential setting of MCLs for carcinogens as MDLs continue to decrease.

Emerging Contaminants - Defining probable exposure levels to Perfluorinated Compounds (PFCs) in the environment should include reference to measured concentrations. The challenge, in the context of policy, is the large number of individual PFCs and determining the relative importance of each of these compounds and whether the measurement and quantification of each compound is necessary. Having one or more indicator compounds for PFCs is one approach, but the prioritization of which compound(s) remains uncertain. The long turn-around-times to obtain results, which typically precludes the ability to collect a high number of samples per field event, suggests that field-based methods for measuring PFC concentrations should be considered. Such on-site measurements would likely focus on a subset of indicator compounds, and may include use of PFC-specific sensors. Collation and evaluation of existing measurement data will inform future method development and account for the plethora of PFC compounds in the environment and, importantly, inform the drive for lower levels of quantification.

Vapour Intrusion - Current practice for vapour intrusion assessment includes measuring concentrations in indoor air using a few (often just two) 24-hour samples collected in two different seasons. The representativeness of this sampling approach is questionable owing to the documented variability in indoor air concentrations, which can space two or more orders of magnitude over short or long time periods. As a result, policies for evaluating vapour intrusion risks range from requiring many more sampling events to use of substantial safety factors to account for the variability. Alternative approaches, such as the mass flux characterization approaches currently seeing increased interest, are needed that can more quickly and more definitively evaluate the potential risks.

REFERENCES

Deshmukh, N., Barker, J., Petroczi, A., and D.P. Naughton. 2011. Detection of Stanozolol in Environmental Water Using Liquid Chromatography Tandem Amss Spectrometry, Chemistry Central Journal, Vol 5, No 1.

EMERGING ENVIRONMENTAL CONTAMINANTS AND CURRENT ISSUES

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INTRODUCTION

Environmental research continues to expand beyond traditional, regulated contaminants to emerging contaminants, such as sucralose and other artificial sweeteners, nanomaterials, perfluorinated compounds, pharmaceuticals, hormones, drinking water and swimming pool disinfection by-products (DBPs), sunscreens/UV filters, brominated flame retardants, benzotriazoles, siloxanes, naphthenic acids, musks, pesticide transformation products, antimony, perchlorate, algal toxins, microorganisms, and new contaminants on the horizon: ionic liquids and prions (Table 1). These are now frequently being found in water samples, including rivers, lakes, ground water, and drinking water. Moreover, understanding their fate and transport in the environment and in wastewater/drinking water treatment is vitally important, and as such, one of the major trends continues to be in identifying their transformation products. Because environmental samples are inherently complex mixtures with trace-level contaminants, the development of sensitive and modern analytical tools has been key for their identification and measurement. This presentation will provide an overview of emerging contaminants and the modern tools used to measure them. This will include a discussion of high resolution (HR) mass spectrometry (MS), liquid chromatography (LC)/MS/MS, gas chromatography (GC)xGC-MS, direct sampling ionization-MS techniques, nuclear magnetic resonance (NMR) spectroscopy, and halogen-specific total organic halogen (TOX) analysis, as well as current extraction technologies.

NEW REGULATIONS AND REGULATORY METHODS

In addition, new regulations and regulatory methods will be discussed. These include the upcoming regulation for perchlorate, as well as other chemicals currently being considered for regulation, including nitrosodimethylamine (NDMA), volatile organic compounds (VOCs), chlorate, and chromium-6. The U.S. EPA's Contaminant Candidate List (CCL)-3, the Draft CCL-4, the Unregulated Contaminant Monitoring Rule (UCMR-3), and the planned UCMR-4, which are priority "watch" lists of chemicals for potential regulation, will also be discussed.

EMERGING CONTAMINANT RESEARCH TRENDS

The analysis of environmental transformation products continues to be a major trend in environmental chemistry, and increasingly, researchers are taking this a step further in proposing complex transformation pathways, with detailed mechanisms deduced by LC/MS/MS and LC/HRMS, and sometimes confirmed by NMR.

Researchers continue to combine toxicology with chemistry, in particular with the testing of transformation products and DBPs for toxicity, but also in effect-directed research to identify unknowns responsible for adverse environmental effects. Examples include the use of androgenic and anti-androgenic assays coupled with LC/HRMS to identify androgen-disrupting compounds in environmental samples; the use of an oxidative stress assay coupled with GC/MS/MS and LC/MS/MS to determine how much of the total oxidative stress response could be attributed to target chemicals measured in environmental waters; the use of multiple endocrine disrupting assays to identify endocrine disrupting compounds (EDCs) in treated wastewater, and the use of a neurotoxicity assay with LC/MS/MS to identify an emerging neurotoxicant in environmental samples.

In the perfluorinated chemical (PFC) area, increasing research is focusing on the aqueous film forming foam (AFFF) formulations used to extinguish fires and also on the lower carbon chain compounds (C4 and C6), which have increased in the environment due to phase-out of higher carbon analogues. In a similar vein, there is also increased investigation of newer flame retardants (both brominated and chlorinated) which have replaced polybrominated diphenyl ethers (PBDEs) in North America and Europe. Trends with artificial sweeteners include their use as markers of wastewater-impacted groundwaters, and new research shows that acesulfame might be a more sensitive marker than sucralose. Nanomaterials continue to be a hot area of research, with fullerenes, nanotubes, quantum dots, metal oxanes, TiO_2 and CeO_2 nanoparticles, nanosilver, nanogold, and zerovalent iron nanoparticles being studied for their environmental fate and presence in the environment. Pharmaceutical presence and fate continues to be a hot topic of interest, with highly toxic chemotherapy drugs being investigated recently, along with an increasing number of pharmaceuticals that show adverse ecological effects at environmentally relevant concentrations. Illicit drugs continue to be found in the environment and are being used forensically to determine drug use in populations. DBPs formed by pharmaceuticals is also a growing trend, with NDMA and highly toxic iodinated DBPs formed by some pharmaceuticals when they react with chlorine or chloramine in drinking water treatment. Algal toxins, which are natural contaminants, continue to be of major concern around the world, and this issue was heightened in the United States last year when a huge algal bloom occurred in the Western part of Lake Erie, temporarily shutting down the drinking water system for Toledo, Ohio. Of the new contaminants on the horizon, ionic liquids are one of the hottest areas in chemistry, due to their use as “green chemistry” replacements to traditional solvents used in industry. However, there is limited toxicity and environmental data for these new “green” solvents, and there is the potential that they may pose a threat to aquatic and terrestrial ecosystems. There is also significant concern regarding the fate and transmission of prions in the environment. These are examples that will be discussed in this presentation.

Table 1. Emerging Environmental Contaminants
Sucralose and Other Artificial Sweeteners
Nanomaterials
PFOA, PFOS, and Other Perfluorinated Compounds
Pharmaceuticals and Hormones
Drinking Water and Swimming Pool Disinfection By-products (DBPs)
Sunscreens/UV Filters
Brominated Flame Retardants
Benzotriazoles
Siloxanes
Naphthenic Acids
Musks
Pesticide Transformation Products
Antimony
Perchlorate
Algal Toxins
Microorganisms
Contaminants on the Horizon: Ionic Liquids and Prions

REFERENCES

Richardson S.D. and Ternes T.A. (2014) Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem*. 86:2813-2848.

NATURE, ENVIRONMENTAL FATE, AND POTENTIAL HUMAN AND AQUATIC TOXICITY OF POLAR METABOLITE MIXTURES IN GROUNDWATER AT BIODEGRADING FUEL RELEASE SITES

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INTRODUCTION

In 2014, CRC Care identified the metabolites of petroleum biodegradation (termed "weathered hydrocarbons" or "polar transformation products") as potential contaminants of emerging concern in their Technical Reports 29 and 31 and recommended that a review of overseas guidance and the best available scientific data be used to evaluate whether guidance or screening levels need to be developed for the metabolites. The Study described herein was conducted in 2011-2014 to provide a detailed understanding of the chemical nature of these metabolites, their environmental fate and potential toxicity to humans and aquatic receptors, thus providing significant information in line with the CRC recommendation. In this Study, groundwater from biodegrading fuel sites was collected and served as real-world samples of petroleum biodegradation metabolite mixtures. The samples were analysed using targeted and non-targeted techniques, and toxicity evaluations of the mixtures were conducted for human and aquatic receptors. Although the Study was conducted using groundwater from fuel release sites in the US, these results should be directly applicable to fuel release sites in Australia. We note that CRC Care cited the initial publications for this Study (Zemo et al 2013, *Groundwater Monit. & Remed. v33n4*; and Mohler et al 2013, *Environ. Sci. Technol. v47*) in its 2014 Technical Reports, but did not describe the results. The Study has expanded significantly since the first publications, and the updated results are presented herein.

METHODS

The potential universe of molecular structural classes for metabolites from biodegradation of petroleum fuels was identified using literature sources: Five "families" (organic acids and esters [combined for this Study], alcohols, ketones, aldehydes, and phenols), and five structural classes within each of four families (n- and alkyl-; cycloalkyl-; polycyclic alkyl-; aromatic-; polycyclic aromatic-) and two classes for phenols (phenol and alkyl-). A human oral reference dose (RfD)-based toxicity ranking system was developed for each of the 22 structural classes of metabolites consistent with systems used by USEPA and United Nations. The ranking system was "Low" (RfD≥0.1 mg/kg/day), "Low to Moderate" (0.1>RfD ≥0.01) and "Moderate" (0.01>RfD≥0.001) toxicity. Groundwater samples were collected from source area and downgradient wells at five fuel terminal sites with highly biodegraded plumes and at five fuel service station sites with less biodegraded plumes. The samples were extracted in triplicate using methylene chloride (DCM); one of the extracts was subjected to silica gel cleanup (SGC) to separate hydrocarbons in the sample (which are relatively non-polar) from the biodegradation metabolites (which are polar), and the silica gel column was rinsed with methanol to elute the polars. The three DCM extracts and methanol eluate for each well were analyzed for: extractable TPH (USEPA Method 8015B); 76 individual "target" metabolites (modified USEPA Method 8270C (GC-MS; quantitative mode)); an open-scan library search using GC-MS; and comprehensive two-dimensional GC-MS (GCxGC-TOFMS) in a "non-targeted" mode. The GCxGC results for the three DCM extracts and the methanol eluate for each well were combined to obtain the widest possible identification of polar compounds. The tentatively identified metabolites for each well were classified into the 22 molecular structure classes and their associated toxicity ranking. Chronic aquatic toxicity tests were conducted on three species using undiluted groundwater from an upgradient well (free of metabolites and hydrocarbons) and a downgradient well (containing metabolites but no hydrocarbons) from 10 representative sites. The testing was conducted by a commercial laboratory using USEPA Methods 1001 [green algae], 1002 [daphnid], and 1003 [fathead minnow]); the concentration of polars in the tested groundwaters (measured as TPH without SGC) ranged from 120 ug/L to 1,800 ug/L.

RESULTS

Initial results from this Study for the first round of terminal samples were published in 2013 (Zemo et al 2013; Mohler et al 2013). The results shown herein include all of the data from terminals and service stations now available. Depending on the location of the sample (source vs. downgradient) and stage of biodegradation, about 70% to 100% of the dissolved organics in the groundwater samples were polar. Virtually all metabolites were tentatively identified after GCxGC analysis; very few of either the target or tentatively identified metabolites were detected using standard GC-MS. The structures of the identified polars were consistent with petroleum biodegradation metabolites; very few non-metabolite polar compounds (e.g., thiophenes) were identified. Naphthenic acids and alkylphenols were infrequently identified. These structures were highlighted as metabolites of potential concern by CRC Care in 2014. For samples without an entrained product component, source area samples from less-biodegraded plumes had about equal per-sample average percentages of ketones (31%) and alcohols (37%), followed by acids/esters (21%), with few aldehydes (7%) and fewer phenols (4%). The source area samples from more-biodegraded plumes had higher per-sample average percentages of acids/esters (45%), followed by ketones (27%) and alcohols (22%), with even fewer aldehydes (6%) and very few phenols (1%). The downgradient samples from more-biodegraded plumes were dominated by acids/esters (63%), followed by alcohols (24%), ketones (12%), aldehydes (1%) and phenols (1%). The most-frequently identified molecular structures in the downgradient samples were simple n- and alkyl- acids/esters. This is evidence that the metabolites themselves naturally attenuate and are biodegraded via sequential oxidation reactions. The vast majority of the metabolites identified in the samples are in structural classes ranked as “Low” toxicity to humans, including in less-mature plumes where elevated concentrations of dissolved aromatic hydrocarbons are still present. The overall trend for the metabolite mixture in groundwater over time with continued biodegradation is toward (1) simpler molecular structures, (2) a higher proportion of organic acids/esters, and (3) an ever-lower human health toxicity profile. Aquatic toxicity testing generally demonstrated no difference in observed toxicity between upgradient samples devoid of metabolites and downgradient samples that contained metabolites. Observed toxicity was mostly attributed to background water quality, and was not correlated to the concentration of polars in the samples.

CONCLUSIONS

Results from this study provide the information requested by the 2014 CRC Care Technical Reports. The complex mixtures of polar metabolites in groundwater from biodegrading fuels are unlikely to pose a significant risk to human health or to aquatic receptors. The toxicity results reported by other investigators for mixtures of biodegradation metabolites from other petroleum sources (e.g., mixtures dominated by naphthenic acids, as studied in Canada) should not be applied to the metabolite mixtures in groundwater from biodegrading fuel release sites. Our results show that naphthenic acids and alkylphenols were very infrequently identified, and thus would be inappropriate “surrogates” for metabolite mixtures. The low-toxicity metabolites from biodegrading fuels (RfDs of 0.1 to 1.0 mg/kg/day) should not be equated to aromatic hydrocarbons (RfDs of 0.03 to 0.04 mg/kg/day) for risk management purposes. If TPH results are to be compared to hydrocarbon-based regulatory criteria, it is important to separate the metabolites in a sample from the hydrocarbons by including a SGC step in the analytical procedures.

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PROVIDING THE INFRASTRUCTURE NEEDED TO IMPROVE THE QUALITY OF PBDE MEASUREMENTS IN AUSTRALIA

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INTRODUCTION

Polybrominated Diphenyl Ethers (PBDEs) are of global concern because of their high toxicity and environmental impact. In 2012, PBDEs were listed as a first-tier priority contaminant for the Australian contaminated land industry as limited information is available on PBDE levels in the environment and the risk they pose (Scott, 2012). In 2013, PBDEs were included in the National Environment Protection Measure (NEPM) for the assessment of contaminated land.

The measurement of PBDEs is technically challenging as these compounds are typically present at trace concentrations and must be quantified against a background of numerous other structurally similar compounds in very complex matrices. Heat and light stability issues further complicate the analysis. Inter-laboratory studies show large analytical variability (22-91%) between laboratories (UNEP, 2014) compromising the reliability of data produced.

The analytical challenges were considered significant and in 2014, the International Bureau of Weights and Measures' Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) conducted a key comparison study (CCQM-K102) for assessing the current state-of-the-art measurement capabilities of National Metrology Institutes (NMIs) for PBDEs analysis. As part of this study, the National Measurement Institute of Australia (NMIA) developed a Reference Measurement Procedure (RMP) for PBDEs in sediment capable of providing high-accuracy reference measurements.

METHODS

Sediment samples were extracted with toluene using Accelerated Solvent Extraction (ASE). Extracts were back-washed with sulphuric acid and water prior to solid phase extraction clean-up. The PBDE congeners were quantified by an isotope-dilution procedure using gas chromatography/high resolution mass spectrometry with certified reference materials as calibrants. Carbon 13-labelled analogues of the congeners were used as internal standards.

RESULTS AND DISCUSSION

Critical aspects of the RMP were thoroughly optimised and validated to minimise potential sources of bias and achieve high accuracy in measurement.

Sample Extraction

Samples were exhaustively extracted to maximise the recoveries of analytes from the matrix as PBDE congeners have a strong affinity for sediment particles and exist as bound analytes. Different extraction solvents and different extraction techniques were tested to determine the best conditions for sample extraction as shown in Table 1.

Table 1. Optimisation of sample extraction conditions

	Mass fraction (ng/g)			
BDE	ASE Toluene	ASE Ethanol/Toluene	ASE Acetone/Hexane	Hot Soxhlet Toluene
47	16.2	16.5	16.6	15.9
99	34.4	35.2	34.4	33.8
153	6.24	6.39	6.20	6.33

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Matrix Interferences

PBDEs in sediment extracts must be well separated from other co-extracted compounds during analysis as interfering responses can produce erroneous results. Sediment extracts were analysed by various chromatography/mass spectrometry techniques that differed in selectivity to assess if matrix interferences were significant in the RMP (Table 2).

Table 2. Comparison of instrumental techniques for sample analysis

	Mass fraction (ng/g)		
BDE	GC-HRMS	GC-MS/MS	LC-MS/MS
47	16.2	15.9	16.5
99	34,4	33.3	33.8
153	6.24	-	6.23

GC: gas chromatography; LC: liquid chromatography; HRMS: high resolution mass spectrometry; MS/MS: tandem mass spectrometry

The differences in the BDE mass fractions determined using different extraction conditions and instrumental techniques were statistically insignificant demonstrating that bias due to incomplete analyte extraction and matrix interferences was minimal in the RMP.

Key Comparison Study, CCQM-K102

NMIs from 15 countries participated in CCQM-K102. The RMPs used by the various institutes differed with respect to sample extraction and clean-up, the instrument methods used for analysis and the calibrants and calibration procedures employed for quantification. Preliminary results of the study showed that the laboratory means were in very good agreement with between-institute relative standard deviations ranging from 6-9%.

Dissemination of Measurement Capabilities

The CCQM study demonstrated the ability of NMIs to produce equivalent measurements despite the complexities associated with PBDEs analysis. One way in which NMIs can disseminate their measurement capabilities to testing laboratories is by providing reference values determined using RMPs for Proficiency Testing (PT) schemes. Currently, a number of international providers offer PT programs for PBDEs analysis and report the consensus mean or median as the target value. There are however, no Australian schemes available (Johnston *et al*., 2013). The reference methodology developed by NMIA could be used to establish the first Australian PT program for PBDEs in environmental samples with reference values assigned to samples. Laboratories will be able to benchmark their performance against the reference values provided and directly assess the accuracy of their methods.

CONCLUSIONS

Reliable data on environmental contaminants is needed for meaningful interpretation of exposure studies and the effective development of policies and regulations. PT is an important tool that laboratories can use to demonstrate the accuracy of their methods and this is best achieved when reference measurements are used as target values for study samples. The availability of an Australian PT scheme for PBDEs analysis with target-setting using a high-accuracy, internationally-recognised RMP developed in Australia will assist laboratories produce measurements that are accurate and reproducible independent of the method used and the laboratory performing the analysis.

REFERENCES

Johnston, L.A., Croft, M.Y., and Murby, E.J., (2013), *Analytical methods for priority and emerging contaminants – a literature review*, CRC CARE Technical Report no. 24, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Scott, K., (2012) Identifying emerging and priority contaminants. Remediation Australasia 9: 12-13.

UNEP Biennial Global Interlaboratory Assessment on Persistent Organic Pollutants, Second Round 2012/2013, June 2014.

DETERMINING POLYBROMINATED DIPHENYL ETHER (PBDE) LEVELS IN URBAN SOILS OF MELBOURNE, AUSTRALIA

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardant that have been incorporated into plastics, electronic equipment, various foams and textiles (NICNAS, 2001). PBDEs have come under a great deal of scientific and regulatory scrutiny due to their long-range atmospheric transport potential (Zhao *et al.*, 2009), persistence in the environment (Litz, 2002; Law *et al.*, 2014) and toxicity (ATSDR, 2004). Ubiquitous contamination of air, soil and sediments has been indicated throughout the world (Law *et al.*, 2014) while adverse effects have been shown in humans and animals from exposure to the substance at environmentally relevant concentrations (ATSDR, 2004). In recognition of this, PBDE formulas Penta-BDE and Octa-BDE were registered as Persistent Organic Pollutants (POPs) under the United Nations Stockholm Convention in 2009 (UNEP, 2009). The remaining product, Deca-BDE, has been officially proposed for registration (UNEP, 2013). Import and use of Penta- and Octa-BDE were banned in Australia in 2007 (NICNAS, 2007) and the National Environment Protection (Assessment of Site Contamination) Measure 1999 was augmented in 2013 to include a health investigation level (HIL) for PBDEs in soil (NEPC, 2013). The objective of this study was to determine the current PBDE contamination status of PBDEs in Australian surface soils to assess the implications of the new NEPM guidelines. An auxiliary aim was to identify PBDE emission sources in the city of Melbourne through a comparison of industrial land concentrations with urban background levels.

METHODS

Twenty-nine surface (0-10 cm) soil samples were collected from Melbourne, Australia. Sample locations were segmented into pollution source classes and land-use categories as follows.

- (a) Manufacture source
  - (i) General chemical manufacture (n=7)
  - (ii) Plastics and foams manufacture (n=11)
- (b) Disposal Source
  - (i) Waste incinerators (n=2)
  - (ii) Electronics recyclers (n=2)
  - (iii) Domestic dumpsites (n=2)
- (c) Non-source
  - (i) Residential (n=2)
  - (ii) Urban parkland (n=2)
  - (iii) University campus (n=1)

Eight PBDE congeners of environmental concern (BDE-28, -47, -99, -100, -153, -154 -183 and -209) were quantified using selective pressurized liquid extraction (S-PLE) and gas chromatography quadrupole mass spectrometry (GC-QqQ-MS).

RESULTS AND DISCUSSION

PBDEs were detected in 28/29 samples with Σ_8PBDE soil concentrations ranging <LOQ-765 ng/g dw and Σ_7PBDEs levels (excluding BDE-209) of <LOQ-50 ng/g dw. The mean Σ_8PBDE

concentration in soils from waste disposal sites was 6 times higher than that of manufacturing industries and 42 times urban background levels. Electronics recycling facilities represented the greatest source of Σ_8PBDE soil contamination. BDE-209 was the dominant congener and contributed 87.9 % of the total mass of Σ_8PBDEs followed by BDE-183, BDE-99 and BDE-47 at 5.5, 3.0 and 1.8 %, respectively.

Table 1 Summary data of PBDE soil concentrations (ng/g dw)

Classification	***n***	**Σ_7PBDEs**			**BDE-209**			**Σ_8PBDEs**		
		mean	min	max	mean	min	max	mean	min	max
Manufacture	18	6.0	<0.14	21	25	<10	114	31	<11	135
Disposal	6	15	0.55	50	187	<10	749	192	2.9	765
Non-Source	5	2.2	0.39	4.7	2.0	<10	12	4.6	0.39	17

CONCLUSIONS

The levels of NEPM restricted congeners measured in this study are substantially lower than the prescribed HIL limit of 1,000 ng/g. The inclusion of BDE-209 within the NEPM HIL framework could be significant as BDE-209 levels were considerably higher than the sum of all other congeners. While greater sample numbers are required to elucidate key PBDE sources to soils, the current data set indicates that electronics recycling facilities are likely to be the most significant contributor of contamination among Victorian land-uses.

REFERENCES

ATSDR (2004) *Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers.* Agency for Toxic Substances and Disease Registry, Atlanta, USA

Law, R. J., Covaci, A., Harrad, S., Herzke, D., Abdallah, M. A. E., Fernie, K., Toms, L. M. L. & Takigami, H. (2014) Levels and trends of PBDEs and HBCDs in the global environment: Status at the end of 2012. *Environment International,* 65**,** 147-158.

Litz, N. (2002) Some investigations into the behavior of pentabromodiphenyl ether (PeBDE) in soils. *Journal of Plant Nutrition and Soil Science,* 165**,** 692-696.

NICNAS (2001) *Polybrominated flame retardants (PBFs): Priority existing chemical assessment report No. 20.* National Industrial Chemicals Notification and Assessment Scheme, Sydney, Australia

NICNAS (2007) *Interim public health risk assessment of certain PBDE congeners contained In commercial preparations of pentabromodiphenyl ether and octabromodiphenyl ether.* National Industrial Chemicals Notification and Assessment Scheme, Sydney, Australia

UNEP (2009) *Stockholm Convention on Persistent Organic Pollutants. Stockholm, 22 May 2001, Adoption of Amendments to Annexes A, B and C. Reference: C.N.524.2009.TREATIES-4 (Depository Notification).* United Nations Environment Program, Stockholm, Sweden

UNEP (2013) *Proposal to list decabromodiphenyl ether (commercial mixture, c-decaBDE) in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants.* Stockholm Convention on Persistent Organic Pollutants, Stockholm, Sweden

Zhao, Y. X., Qin, X. F., Li, Y., Liu, P. Y., Tian, M., Yan, S. S., Qin, Z. F., Xu, X. B. & Yang, Y. J. (2009) Diffusion of polybrominated diphenyl ether (PBDE) from an e-waste recycling area to the surrounding regions in Southeast China. *Chemosphere,* 76**,** 1470-1476.

EMERGING CONTAMINANTS UPDATE, WITH A FOCUS ON PER- AND POLYFLUOROALKYL SUBSTANCES AND 1,4-DIOXANE

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INTRODUCTION

Emerging contaminants (ECs) are compounds with a real or perceived threat to human health and the environment but that lack a promulgated health standard or have evolving standards. Discovery of ECs at established remediation sites can have a profound impact on the schedule, cost, and effectiveness of remediation programs. Familiarity with the process by which chemicals become regulated compounds is an important step in understanding and managing emerging contaminants.

SAMPLING CONSIDERATIONS

ECs are generally characterized by lower health advisory levels and lower analytical quantitation limits than the environmental industry has customarily dealt with over the past several decades related to common site contaminants. For instance, established standards for common groundwater contaminants (e.g., trichloroethene, benzene) are in the range of 5 micrograms per liter (µg/L or parts per billion - ppb), whereas several emerging contaminants have health advisory levels that are in the 10's to 100's of nanogram per liter (ng/L or parts per trillion - ppt) range. Widespread, low-level occurrence of certain ECs may not be site-specific, but could be related to atmospheric deposition. The discovery of low levels of ECs at a site could drive remediation decision-making, or at the very least could require significant sampling efforts to demonstrate whether they are site-related or not. Application of a robust decision-making process prior to sampling ensures that likely contaminants are properly identified, but also avoids unnecessary sampling time and expense. A decision process will be presented herein which allows a rational and well-considered approach to be followed in determining when sampling is warranted and when it is unlikely to lead to useful information. This process will be demonstrated using 1,4-dioxane (1,4-DX) and per- and polyfluoroalkyl substances (PFAS), two ECs of particular interest at present.

Sampling and analysing to characterize EC impacts at the low levels required has the potential to introduce false positive results due to interference from sampling equipment or decontamination detergents containing trace levels of target compounds. False negative analytical results could also result from sorption of the target compounds on either sampling or lab analytical equipment. This presentation will briefly identify sources of false positive and false negative results that may impact findings and conclusions for two common emerging contaminants: PFAS and 1,4-DX. Many sampling pumps contain or are coated with fluoropolymers and fluorotelomers, such as polytetrafluoroethylene (PTFE). Internal parts include O-rings, seals, impellers, bladders, and wire jackets. Sample tubing is often coated as well. Many of these parts contact the groundwater sample during collection and have the potential to introduce low-level contamination that may be incorrectly attributed to the facility or aquifer. In a leaching sample from a common environmental detergent that was collected in February 2013, 1,4-DX was identified at 760 J µg/L. This sample was not representative of the concentrations that would be present if a manufacturer's recommended 1% solution was prepared, and then triple-rinsed off the sampling equipment. But it still raises a concern that low level 1,4-DX detections could be due to residual soap on the sampling device.

CHEMISTRY, OCCURRENCE AND REMEDIATION OF 1,4-DIOXANE AND PFAS

A variety of recent information related to the chemistry, occurrence, and applicable remediation technologies will be provided, including a summary and evaluation of the US EPA Unregulated Contaminant Monitoring Rule 3 (UCMR3) drinking water supply system sampling results for 1,4-DX and PFAS. A surprisingly high frequency of detections were exhibited in the data suggesting much more widespread occurrence than was previously anticipated for these two ECs of interest. Details will be presented addressing possible sources and an assessment of the number of sites that may be revealed by this sampling in the future. Additional recently published information regarding the co-occurrence of 1,4-DX and various chlorinated solvents will be reviewed and implications discussed.

The cutting edge of 1,4-DX and PFAS remediation technologies will be summarized, including lab, bench, field pilot scale testing and full-scale implementation. Considerable research is being conducted at present for both of these ECs, with most 1,4-DX treatment technologies having advanced from the lab to the field pilot and recently to full-scale implementation. Demonstrated technologies for both in situ and ex situ treatment of 1,4-DX are dominated by oxidation approaches, including ozone/hydrogen peroxide, alkaline activated sodium persulfate and catalyzed hydrogen peroxide. Biological approaches, including assessment of intrinsic bioremediation and enhanced natural attenuation, have recently been demonstrated utilizing co-metabolic processes driven by gasotrophic bacteria, such as propanotrophs. Microbiological tools are being developed at several academic research labs to allow more consistent and credible assessment of natural process and reactions to stimulants.

Remediation of PFAS is proving significantly more problematic for the industry, with attempts at chemical reductive and oxidative destruction, sorption, and biodegradation being made by university researchers and amendment suppliers. For the most part, these attempts have failed to demonstrate complete destruction of the most commonly evaluated PFASs and their associated precursors. The state of the remediation industry and marginal successes will be reviewed and recent and ongoing research briefly presented.

KEY ISSUES REGARDING THE FATE AND TRANSPORT OF EMERGING CONTAMINANTS

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INTRODUCTION

The environmental industry is continuously challenged with new and emerging compounds that pose a real or potential health or environmental risk. To address this challenge, improved insight into the nature of the compound, its behavior in the environment, and its susceptibility to natural and enhanced degradation processes are typically needed. Regardless of the emerging compound of interest, many of the same key issues often need to be understood in order to address uncertainties regarding risk and treatment.

For this study, three emerging compounds (or, classes of emerging compounds) were selected. These compounds include perfluorinated compounds, for which perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were selected as model compounds due to the regulatory emphasis currently placed on PFOA and PFOS in the United States, 1,4-dioxane, and ethylene dibromide (EDB). These compounds have all impacted (or, potentially impacted) a large number of sites, are relatively mobile in groundwater, have limited or undetermined intrinsic degradation under typical conditions, and are recalcitrant to many conventional treatment technologies.

METHODS

Key issues regarding the fate and transport of perfluorinated compounds, 1,4-dioxane, and EDB can be considered to fall into the 5 general categories shown in Figure 1. Fate and transport processes associated with the primary source area and/or low permeability regions typically control the longevity and intensity of dissolved plumes, while attenuation processes in the primary flow paths of the plume mitigate the contaminant flues emanating from source or low permeability zones. The presence of co-contaminants or application of remedial amendments to facilitate contaminant transformation also are key issues with respect to the fate and transport of these emerging contaminants. Finally, as indicated by the items in the center of Figure 1, contaminant fate and transport can be impacted by a wide range of coupled physical, chemical, and biotic processes.

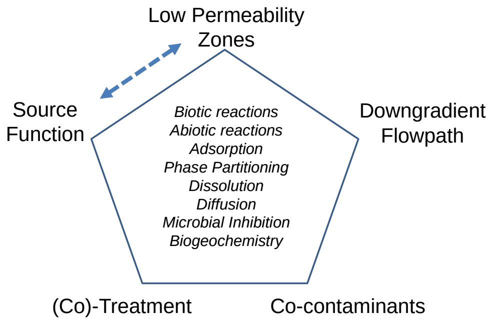

Fig. 1. Key areas for assessing fate and transport for emerging contaminants.

To illustrate the importance of the processes in Figure 1, and the current data gaps in understanding for the selected emerging contaminants, source functions for PFOA/PFOS and EDB were considered, particularly with respect to phase partitioning. In addition, abiotic EDB dehalogenation reactions in low permeability materials were investigated. Finally, the impacts of co-contaminants on the biodegradation of 1,4-dioxane were considered. All of these fate and transport processes were considered with respect to data gaps and potential impacts on field-scale processes.

RESULTS AND DISCUSSION

PFOA/PFOS Source Function

Our recent investigation of a perfluorinated compound source area showed that non-aqeuous phase liquids (NAPLs) often may be present with PFOA/PFOS sources (McGuire et al., 2014). Due to the surfactant nature of PFOA and PFOS, the NAPL architecture likely impacts the interfacial sorption of these compounds, thus greatly impacting the apparent NAPL-water partitioning and source strength function. The importance of this mechanism has been demonstrated in recent laboratory-scale studies (Guelfo and Higgins, 2013.

EDB Source Function

While Raoult's Law has been used to estimate partitioning of EDB from a NAPL source to groundwater, this may be a poor approximation for the EDB source function. Difference in chemical structure between EDB and the hydrocarbons found in NAPL, as well as weathering of the NAPL, limit the usefulness of applying Raoult's Law.

Abiotic Dehalogenation of EDB in Low Permeability Materials

Laboratory testing has shown that EDB is amenable to abiotic dehalogenation reactions in low permeability matrices. These ferrous-iron induced reactions, while slow, will likely impact the long-term fate and transport of EDB at impacted sites. However, these reactions remain poorly understood.

Impacts of Co-Contaminants on Biodegradation of 1,4-dioxane

Recent studies have shown that the biodegradation of 1,4-dioxane can be impacted by the presence of chlorinated solvents and/or their metabolites. Thus, when considering bioremediation for 1,4-dioxane, the presence of co-contaminants needs to be considered when estimating remedial timeframes.

CONCLUSIONS

This study has clearly shown that many of the key fundamentals needed to understand the fate and transport of PFOA/PFOS, 2,4-dioxane, and EDB are lacking. Additional research is needed to further explore the processes identified in this study so that improved assessment, management, and (when needed) remediation of impacted groundwater can be attained.

REFERENCES

J.L. Guelfo, C.P. Higgins, Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites, Environ. Sci. Technol. 47 (2013), 4164-4171.

M. E McGuire, C. Schaefer, T. Richards, W. J. Backe, J. A. Field, E. Houtz, D. L. Sedlak, J. Guelfo, A. Wunsch, C. P. Higgins, Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance (PFAS) Distribution at a Former Firefighter Training Area, Environ. Sci. Technol. (2014), DOI: 10.1021/es5006187.

RISK-BASED MANAGEMENT AND REMEDIATION OF BENZO(A)PYRENE

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INTRODUCTION

Benzo[a]pyrene (B(a)P) has been identified by CRC CARE as a first tier priority contaminant (CRC CARE 2014) in Australia, and is classified by the US EPA as a priority pollutant due to its probable carcinogenicity. B(a)P is a common contaminant throughout Australia, ubiquitous in the urban, and to a lesser extent, regional environments.

Although numerical screening levels for human health and the environment are available in Australia, these are stringent and often exceeded. The bioavailability of B(a)P varies considerably depending on the presence of other PAHs, the matrix, the age of contamination and so forth, and is difficult to measure. The application of the published investigation and screening levels is reasonably well understood, although to date it has generally not been possible to vary these levels to account for bioavailability even though it is suspected that B(a)P will not be bioavailable in many situations.

In terms of management and remediation of B(a)P contamination, reasonably well understood methods of remediation are available such as physical-chemical treatment, thermal treatment, and landfill disposal. There are other potentially lower costs methods of treatment that are often considered, but are not well understood.

CRC CARE has commenced a project to provide guidance on the risk-based management and remediation of B(a)P, and has formed a working group comprising representatives of regulatory agencies, industry and research organisations. The objective of this project is to develop guidance that accounts for site-specific variables such as bioavailability, bioaccumulation and the exposure that will occur. It is intended that this guidance will assist practitioners, regulators and site owners to effectively manage and remediate B(a)P-contaminated soil and groundwater, and will allow more targeted remediation and potentially reduce the cost of managing BaP contaminated soil and groundwater.

It is expected that draft guidance will be prepared later in 2015, and will be circulated for industry review.

PREPARATION OF GUIDANCE ON THE MANAGEMENT AND REMEDIATION OF B(a)P

The presentation will outline the direction of the work, key areas of focus, and a summary of the guidance that has been developed to date. Key areas are noted in Table 1.

Table 1. Key areas of focus in the development of the Guidelines for B(a)P

Topic	Well understood aspects	Key gap and focus
Health based investigation levels	NEPM HILs	Determining and applying bioavailability
Ecological investigation levels	NEPM ESLs	Determining and applying bioavailability and bioaccumulation considerations
		Guidance on applying commercial/ industrial screening levels
Groundwater concentrations	Determined by direct measurement	Do not attempt to predict from leaching measurements
Decision framework	National Remediation Framework being developed by CRC CARE	Adopt approach that is consistent with the NRF
Soil remediation	Institutional controls, removal and disposal, containment, solidification/ stabilisation, ex-situ treatment (eg thermal) generally well understood	Assessing potential for and acceptability of: beneficial reuse; solvent flushing/ oxidation; biological treatment; in-situ heating; smouldering
Groundwater remediation	Source removal	Assessing potential for and acceptability of in-situ physical/chemical treatment

INVESTIGATION OF EMERGING CONTAMINANTS IN ENVIRONMENTAL WATERS

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INTRODUCTION

Emerging contaminants, such as pharmaceuticals, are a growing environmental concern. These contaminants have been detected in environmental waters (such as surface water, ground and wastewater flows) at concentrations ranging from µg L^{-1} to ng L^{-1} level (Fatta-Kassinos et al. 2011). The majority are unregulated in the environment and as a result the risk assessment and eco-toxicological effect of the contaminants, their metabolites and/or transformation products are relatively unknown (Matamoros et al. 2012). There are several major concerns regarding the presence of pharmaceuticals in environmental waters and include the development of bacterial resistance, the uptake of pharmaceuticals by plants, and the exposure of aquatic organisms to pharmaceuticals (Rodriguez-Mozaz et al. 2007).
To meet the prerequisite of proper monitoring and risk evaluation of emerging contaminants, the development of a sensitive multi-residue screening analytical method for emerging contaminants in complex environmental matrices was undertaken.

METHODS

The first part of the study involved the development and validation of a UHPLC-QTOF-MS (Agilent 6550 iFunnel Q-TOF LC/MS) method for the analysis of a mixture of pharmaceuticals in water. The second part of the study, the method was expanded to include an on-line solid phase extraction (SPE) pre-concentration step.

Standards

All pharmaceutical standards were analytical grade. 17-α-ethinylestradiol, 17-β-estradiol, atenolol, atorvastatin, caffeine, carbamazepine, chloramphenicol, diclofenac, erythromycin, estriol, estrone, fluoxetine, gemfibrozil, ibuprofen, triclosan, ketoprofen, mestranol, naproxen sodium, phenytoin, sulfamethoxazole, and tris(2-carboxyethyl)phosphine, were purchased from Sigma-Aldrich (Australia).

RESULTS AND DISCUSSION

(a) Section I: UHPLC-QTOF-MS method

(i) Different mobile phases were trialled to improve MS-detectability of the target compounds. Ultimately, ACN/water with formic acid in positive ESI mode and ACN/water with no modifiers in negative ESI mode were selected as the operating mobile phases.

(ii) ESI source parameters were varied on a step by step manner to yield optimal parameter values.

(iii) The limits of detection (LODs) were determined through a series of replicate injections at different concentration levels. The residual standard deviation of the regression line of the generated calibration plots was used to calculate the LOD. LODs ranged from 32-494 µg L^{-1} ($\bar{x}$ = 116 µg L^{-1}).

(iv) Accuracy was studied through seven determinations at three concentration levels of spikes in water samples. Concentration levels were selected to encompass the low range of linearity, the middle, and near the high end of linearity based on the calibration plots (i.e. 250, 500 and 750 µg L^{-1}). The precision and trueness are summarised in Table 1.

(b) Section II: Online SPE UHPLC-QTOF-MS method
   (i) Different mobile phases were trialled for the load and wash step with methanol selected as the most ideal. The flow rates and volumes were also optimised.
   (ii) The LODs were calculated in a similar manner to Section I, with LODs mostly in the low ng L^{-1} range. The method detection limit (MDL) averaged 10 ng L^{-1}.
   (iii) The precision and trueness are summarised in Table 2.
   (iv) The method was applied to real water samples taken up and down stream of an undisclosed secondary treatment plant (STP) in Victoria, Australia. Target compounds including atenolol, erythromycin and phenytoin were identified.
   (v) Future directions include the use of labelled internal standards to correct for matrix effects and improve accuracy.

(c) Section III: Exploratory experiments
   (i) pH modifiers and derivatisation agents were briefly explored, with ammonium hydroxide observed to improve the detection of some estrogenic compounds in formic acid carrier.
   (ii) Preliminary experiments to search water sample data (post target analysis) for transformation products yielded tentative hits, although confirmation by additional experiments is necessary.

Table 1. Average method precision and trueness for the online SPE UHPLC-QTOF-MS method.

Run mode:	Positive ESI mode		Negative ESI mode	
Level	**RSD /%**	**Recovery /%**	**RSD /%**	**Recovery /%**
50 ng L^{-1}	8.1	85	8.8	93
250 ng L^{-1}	8.1	86	4.3	68
500 ng L^{-1}	3.2	68	3.4	60

CONCLUSIONS

A working on-line SPE UHPLC-QTOF-MS method has been developed and validated for the sensitive multi-residue analytical method for the analysis of pharmaceuticals in environmental waters. The method has successfully analysed standards in Type I water, and was carried over with relative success to wastewater flows. Applications of this method to further environmental water studies could yield qualitative and quantitative information on emerging contaminants, and their transformation products.

REFERENCES

Fatta-Kassinos, D., Meric, S., Nikolaou, A. (2011), Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research, *Analytical and bioanalytical chemistry*, vol. 399, no. 1, pp. 251-275.

Matamoros, V., Salvadó, V. (2012), Evaluation of the seasonal performance of a water reclamation pond-constructed wetland system for removing emerging contaminants, *Chemosphere*, vol. 86, no. 2, pp. 111-117.

Rodriguez-Mozaz, S.; Lopez de Alda, M. J.; Barceló, D. (2007), Advantages and limitations of on-line solid phase extraction coupled to liquid chromatography–mass spectrometry technologies versus biosensors for monitoring of emerging contaminants in water, *Journal of chromatography*, vol. 1152, no. 1, pp. 97-115

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APPLICATION OF SITE SPECIFIC ADSORPTION ISOTHERMS FOR DERIVING SOIL REMEDIATION GOALS PROTECTIVE OF GROUNDWATER – TOOWOOMBA GASWORKS CASE STUDY

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INTRODUCTION

Soil remediation goals for contaminated sites are typically based on exposure pathways related to human health (e.g. vapour intrusion, direct contact, ingestion etc.). However, in areas where potable quality aquifers are present, soil remediation to levels that are protective of the local groundwater resource, or groundwater-dependent ecosystem, may be required. This particular pathway is not defined by existing Australian guidance due to the uncertainties and complexities associated primarily with this pathway.

One of the key sources of uncertainty is the chemical specific soil-to-water partitioning coefficient (KD), which are derived differently for organics and inorganics and can range widely in the published literature. The level of conservatism necessary to address this uncertainty can often lead to remediation targets which are more stringent than they need be; and consequently and unnecessarily increasing remediation timeframes and costs.

The Toowoomba Gasworks site overlies the Toowoomba Basalt, a potable aquifer, which is used for urban water supply. The site soils were contaminated with ammonia, benzene, petroleum hydrocarbons, and naphthalene. Soil cleanup targets protective of the underlying basalt aquifer were required as part of the remediation works. In order to minimise uncertainty and develop realistic remediation goals, GHD in conjunction with ALS laboratories developed a soil column leaching method designed to rapidly produce high quality data for constructing adsorption isotherms.

The isotherms were used as a basis for deriving site specific KD values, which were then used to produce site specific remediation goals. The application of site specific adsorption isotherms significantly assisted in timely and effectively remediating the site.

METHODS

Based on a throrough review of leach test methods (i.e. WSDEC, 2003), a modified leaching method was developed to provide high quality data for isotherm construction. The method allowed for soil samples to be taken at regular intervals of each of leaching columns for characterising adsorbed phase concentrations.

Numerous data points were generated for various chemicals, including the main chemicals of interest, ammonia, benzene, TPHs, and naphthalene. The isotherms were used to derive site specific KD values, which were then used in infiltration, mixing, and dilution analytical models to conduct a tiered groundwater risk assessment.

RESULTS AND DISCUSSION

The Tier 1 level risk assessment was based on simple comparison between leach test results (i.e. pore water) and soil and groundwater screening criteria, and indicated numerous exceedances of soil cleanup criteria for all areas of interest. This led to Tier 2 risk assessment based on site specific KDs and partitioning, according to following:

$$RT_s = C_S = C_T\left(K_d + \frac{\theta_w + \theta_a H}{\rho}\right)$$

Where RT_S = soil remediation target (mg/kg); C_s = soil conc.(mg/kg); C_T = target soil conc. (mg/kg); K_d = partition coefficient; Θ_w= water-filled porosity; Θ_a= air-filled porosity; H = Henrys Law Constant; and ρ = soil bulk density (g/cm^3).

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Most isotherms for organics followed a linear relationship, while ammonia followed a non-linear Freundlich-type relationship. Figure 1 is an example isotherm based on ammonia, showing both linear and Fruendlich type isotherms. The derived KD value for ammonia was equal to 1809 L/kg. This compares to a KD value of 0.003 L/kg based on published KOC values (TRRP, 2008) and an foc of 0.001.

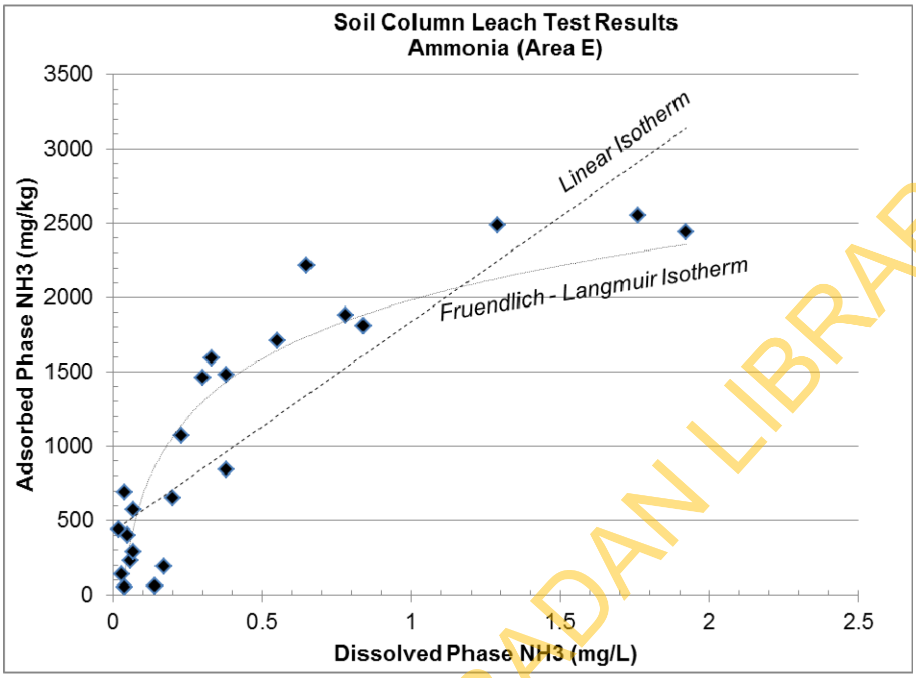

Fig. 1. Adsorption Isotherm for Ammonia, Area E

The site specific KDs for organics (and inorganics such as ammonia) were at least two orders of magnitude greater than published literature values, and Tier 2 and 3 risk assessment based on the UKEA (2006) methodology indicated low impact to groundwater and off-site receptors, which was supported by the age of the site and groundwater data.

CONCLUSIONS

Derivation of site specific KD values using adsorption isotherm data resulted in KDs much higher than published literature values, highlighting the conservatism of the latter and complexity of the soil-to-groundwater pathway. Derivation of site specific KDs via adsorption isotherms accounts for these complexities and allows for more realistic soil cleanup goals for this pathway.

REFERENCES

Texas Risk Reduction Program (2008). Toxicity Factors and Chemical/Physical Parameters. http://www.tceq.state.tx.us/assets/public/remediation/trrp/trrptoxchph042308.xls.
United Kingdom Environment Agency (2006). Remedial Targets Methods.
Washington State Department of Ecology (2003). An Assessment of Laboratory Leaching Tests for Predicting the Impacts of Fill Material on Ground Water and Surface Water Quality – A Report to the Legislature. Toxics Cleanup Program, Olympia, Washington.

REVIEW OF ECOLOGICAL INVESTIGATION LEVELS FOR TOTAL PETROLEUM HYDROCARBONS

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INTRODUCTION

The recent amendment to the National Environment Protection (Assessment of Site Contamination) Measure included some ecological screening values for soil for total petroleum hydrocarbons (TPH) which were based on the Canadian approach. There are many sites with petroleum hydrocarbon contaminated so this addition to the suite of soil guidelines was helpful.

Information is available from CCME and RIVM that is being adapted for use in relation to criteria that may be used to evaluate TPH in soil and surface/ground waters. The way in which the available information on ecological effects for TPH in soil and water is being interpreted has been questioned by auditors/regulators.

RESULTS AND DISCUSSION

A review has been undertaken by enRiskS to work through the latest information available to attempt to recalculate the TPH soil ESLs and to derive a criteria relevant for surface waters for consideration by the NEPM Working Group (representatives of the various EPAs). The review and the revised calculations will be presented.

RISK-BASED SCREENING CRITERIA FOR PCR USE OF WATER: IS 10 TIMES THE DRINKING WATER GUIDELINE PROTECTIVE?

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INTRODUCTION

When assessing human health risk associated with groundwater or surface water pollution, the potential for users to be exposed to contaminants during primary contact recreation (PCR) uses (e.g. swimming in a surface water body or use of bore water to fill swimming pools) must often be assessed. With respect to screening levels for PCR exposure, relevant Australian guidance documents (e.g. NHMRC 2008, ANZECC/ARMCANZ 2000) state that:

- Drinking water guideline (DWG) values can be useful as a guide to deriving screening levels for recreational water use; and
- In some cases a 10-fold adjustment factor (upwards) can be applied to the DWG to account for the 2 litres per day water consumption assumed for derivation of the DWG, relative to the expected 100-200 mL per day consumption during PCR activities.

However, both NHMRC (2008) and ANZECC/ARMCANZ (2000) also point out that the potential for contaminant exposure via non-ingestion routes (e.g. dermal absorption, volatile or aerosol inhalation) must also be considered when assessing risk during PCR use. Thus, the extent to which application of a 10-fold factor to the DWG is protective of PCR users will depend on individual chemical properties: primarily volatility, dermal absorption potential, and relative toxicity via the inhalation vs. oral routes.

As a result, a number of regulators and auditors have routinely raised questions as to whether application of a 10-fold adjustment factor to all chemicals is suitably protective. The objectives of this paper were therefore to derive PCR risk-based screening criteria for a range of inorganic and organic contaminants commonly encountered at Australian contaminated sites, and to compare the derived criteria to DWGs in order to assess the suitability of a default 10-fold adjustment.

METHODS

Risk-based screening criteria were derived for a range of inorganic and organic contaminants most commonly encountered at Australian contaminated sites. The derivation utilised currently recognised and recommended health risk assessment methodology (e.g. enHealth 2012, NEPC 2013), and reasonable upper bound exposure assumptions to assess relevant and complete exposure pathways (incidental water ingestion, dermal absorption and inhalation of volatiles and/or aerosols).

For the purposes of comparison, chemical-specific oral toxicity criteria were assumed to be the same as those utilised for derivation of the drinking water guideline to which the PCR guideline would be compared. Adopted inhalation toxicity criteria were those endorsed by the NEPM (NEPC, 2013), where available, or published by other national or international bodies recognised by NEPC (2013) and enHealth (2012).

RESULTS AND DISCUSSION

A selection of the derived PCR screening criteria are summarised and compared to relevant DWGs in Table 1 below. As shown, the PCR criteria range from approximately 3 to 100 times higher than relevant DWGs.

Table 1. Selected Risk-based PCR Screening Criteria vs. Drinking Water Guidelines

Chemical	PCR Criteria (mg/L)	DWG (mg/L)*	Adjustment Factor
Petroleum Hydrocarbons			
Benzene	9.56E-02	1.00E-03	96
Toluene	2.60E+01	8.00E-01	32
Ethylbenzene	8.72E+00	3.00E-01	29
Xylenes (total)	1.59E+01	6.00E-01	26
Naphthalene	1.60E+00	4.00E-01	4
Chlorinated Hydrocarbons			
Trichloroethylene	7.31E-02	1.00E-02	7
Tetrachloroethylene	1.28E+00	5.00E-02	26
Dichloroethene, cis-1,2-	1.42E+00	6.00E-02	24
Vinyl chloride	3.25E-03	3.00E-04	11
Other Organics			
Benzo(a)pyrene	9.34E-05	1.00E-05	9
DDT	2.99E-02	9.00E-03	3
Metals			
Arsenic	2.05E-01	1.00E-02	20
Cadmium	6.55E-02	2.00E-03	33
Chromium(VI)	1.81E-01	5.00E-02	4
Mercury	5.65E-02	1.00E-03	56

* Primarily sourced from NHMRC (2011).

Key factors which affected the relative difference between PCR and DWG values for different chemicals were the following:

- Chemical volatility (and hence the extent to which vapour exposure during swimming may occur).
- Relative toxicity via the oral, inhalation and dermal pathways.
- Physical-chemical properties, primarily the dermal permeability constant (Kp) which describes the rate at which a chemical can migrate through the skin.
- Methodology used for derivation of the DWG, in particular the percentage of acceptable daily intake that was allocated to drinking water exposure relative to background levels assumed in the PCR criteria derivation.

CONCLUSIONS

Application of a 10-fold adjustment to the relevant DWG in order to assess risks associated with PCR use of water is protective for the majority of, but not all, chemicals. Overall, a 10-fold (or higher) adjustment is likely protective for inorganic chemicals that are not dermal irritants or readily absorbed dermally, but not necessarily appropriate for volatile organic chemicals and/or those with very high Kp values.

REFERENCES

ANZECC & ARMCANZ, 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality,* National Water Quality Management Strategy Document 4: Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

enHealth (2012). *Environmental Health Risk Assessment: Guidelines for assessing human health risks from environmental hazards,* Publication No. DO702: Environmental Health Standing Committee.

NEPC (2013). *National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013 (No. 1),* Canberra: National Environment Protection Council.

NHMRC (2008). *Guidelines for Managing Risks in Recreational Water,* Canberra: National Health and Medical Research Council.

A CASE FOR HIL E — HEALTH INVESTIGATION LEVELS FOR INDIGENOUS AUSTRALIAN COMMUNITIES LIVING A TRADITIONAL LIFESTYLE

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INTRODUCTION

Four generic land use scenarios are used to derive the health investigation levels (HILs) outlined in the NEPM (1999). HILs are based on the types of land use, the sensitivity of the population, and the frequency and intensity of exposure to the soil contaminants. The land use scenarios to which the HILs apply, are intended to be based on typical settings in Australia under which people may be exposed to contaminated soil. The assumptions made within each land use scenario relating, in particular, to the frequency and intensity of exposure to contaminants through exposure pathways may not be applicable to Indigenous Australians, particularly those living a traditional lifestyle, where prolonged periods of time may be spent outside in close contact with the ground while socialising, working, preparing food, and sleeping.

This research presents an exposure scenario that reflects the traditional lifestyles of Indigenous Australians and the need to establish an additional land use scenario, colloquially referred to as 'HIL E.' The traditional lifestyle exposure pathway scenario aims to include consideration of Indigenous Australians within the National Environmental Protection Measure Framework.

METHODS

The land use scenario 'HIL A – low density residential' was used as the base scenario, and the exposure parameters examined to see which, if any, may require modification. The following exposure parameters were initially identified as potentially requiring modification based on broad reading of the literature, and a lay-person understanding of constituents of a traditional Indigenous Australian lifestyle:

- Incidental ingestion of surface soil and dust particulates,
- Dermal contact with surface soil and dust particulates, and
- Outdoor inhalation of dust particulates.

Values are then determined for each exposure parameter, which are then used to calculate HILs.

Information was gathered from Indigenous Australians via semi-structured surveys, supplemented with review of studies undertaken with respect to indigenous populations in living subsistence lifestyles in other countries, to determine similarities or differences in the exposure parameter values. The questionnaire collected information which enabled direct comparison with the exposure parameters values utilised within the NEPM to calculate HILs, i.e. soil/dust ingestion rate, time spent outside, and time spent indoors.

RESULTS AND DISCUSSION

Results from the survey and comparative literature found differences in the exposure parameter values considered as follows:

- Soil and dust ingestion rates were found to be significantly higher than those considered in HIL A.
- Time spent outside was greater than considered in HIL A.
- Time spent indoors, was significantly less, and inversely proportional to time spent outside.

This research has important implications for Indigenous Australians, who may be affected by application of HIL A investigation levels during the initial assessment of a potentially contaminated site. The assumptions underlying the derivation of HIL A do not reflect the lifestyle and living conditions of Indigenous Australians, and may not be sufficiently conservative, potentially presenting an unidentified risk to human health from chronic exposure.

CONCLUSIONS

This research presents an exposure scenario that reflects the traditional lifestyles of Indigenous Australians and the need to establish an additional land use scenario, colloquially referred to as 'HIL E.' Establishment of an additional land use scenario would ensure that Indigenous Australians are considered within the National Environmental Protection Measure Framework.

DEVELOPING GROUNDWATER TIER 1 SCREENING CRITERIA FOR CHRONIC AND ACUTE VAPOUR RISKS FOR CHLORINATED HYDROCARBONS

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INTRODUCTION

For sites with complex chlorinated hydrocarbon groundwater contamination, it can be important to have a preliminary understanding of the likelihood concentrations warrant immediate action or further investigation prior to the collection of soil vapour and/or indoor air data. Australian specific vapour intrusion screening guidelines are not available in the NEPM (1999) for groundwater other than petroleum hydrocarbons.

METHODS

In order to screen groundwater data, screening levels were developed using the United States Environmental Protection Agency (USEPA) (2014) method. This method takes into consideration air concentrations protective of health, the steady state chemical concentration in soil vapour near the groundwater table (using chemical-specific Henry's Law constants), and the attenuation of vapours between a groundwater concentration and the concentration in indoor air. The use of a default attenuation factor of 0.001 is considered to be appropriate to account for attenuation between the soil vapour near the groundwater table and air (USEPA, 2014).

This method was used for screening both potential chronic and acute risks. The difference between applications is the input of chronic versus acute target air concentrations. Target air concentrations for chronic risks were obtained from:

a) National Environment Protection Measure (NEPM) (1999). National Environmental Protection (Assessment of Site Contamination) Measure 1999 (As updated April 2013, NEPC, Canberra);
b) World Health Organisation (2000) Guidelines for Air Quality;
c) United States Environmental Protection Agency (USEPA), March 2010: Region 9 Preliminary Remediation Goals (PRGs) for ambient air; and
d) Dutch Rijksinstituut voor Volksgezondheidt en Milieu (RIVM), 2001: Re-evaluation of human-toxicological maximum permissible risk levels, Dutch National Institute of Public Health and the Environment.

Target air concentrations for acute risks were obtained from:

a) Agency for Toxic Substances and Disease Registry (ATSDR) 2013 Minimal Risk Levels; and
b) USEPA (2014) Acute Exposure Guideline Levels.

RESULTS AND DISCUSSION

A comparison of the screening criteria developed with a groundwater analytical data set for a site with multiple chlorinated hydrocarbons groundwater plumes indicated that there were potential chronic indoor air risks but unlikely to be unacceptable acute risks which required immediate management. Based on these preliminary results further site assessment was able to focus on collection of soil vapour and rule out the need to immediately sample indoor air. The findings of the acute risk assessment to workers from chlorinated hydrocarbon compounds were subsequently validated with the collection of sub-slab vapour data. The sub-slab vapour data confirmed that the approach was acceptable.

CONCLUSIONS

The method used to calculate groundwater screening criteria from indoor air target concentrations is an effective approach to provide an initial assessment of whether immediate actions to assess of current exposure through indoor air or workplace air monitoring is warranted. In addition, further soil vapour site characterisation support the groundwater screening approach did not under-predict potential risk.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR) 2013 Minimal Risk Levels

Dutch Rijksinstituut voor Volksgezondheidt en Milieu (RIVM), 2001: Re-evaluation of human-toxicological maximum permissible risk levels, Dutch National Institute of Public Health and the Environment.

NEPM (1999). National Environment Protection (Assessment of Site Contamination) Measure. As updated per the Amendment Measure 2013 (No. 1). National Environment Protection Council.

United States Environmental Protection Agency (USEPA), (2010) Region 9 Preliminary Remediation Goals (PRGs) for ambient air.

USEPA (2014). Vapor Intrusion Screening Level (VISL) Calculator: User's Guide. Office of Solid Waste and Emergency Response. Washington, DC. May.

USEPA (2014) Acute Exposure Guideline Levels.

World Health Organisation (2000) Guidelines for Air Quality.

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NATIONAL GUIDANCE FOR EMERGING CONTAMINANTS AT CRC CARE

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INTRODUCTION

First tier priority contaminants are the primary focus of CRC CARE guidance development projects on contaminants of emerging concern in the short to medium term (CRC CARE 2014a). The systematic and structured processes for prioritisation of issues, gap analyses, literature reviews, stakeholder engagement and guidance development undertaken at the national level represent some of the best practices in policy development.

The contaminants were identified for CRC CARE through a Forum held in 2012. Based on preliminary literature reviews (CRC CARE 2014b; CRC CARE 2013), CRC CARE commenced projects on developing guidance for perfluorinated chemicals perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), methyl tertiary-butyl ether (MTBE) and benzo[a]pyrene (B[a]P). Further projects are being scoped for weathered hydrocarbons and polybrominated diphenyl ethers (PBDE).

The National Environment Protection (Assessment of Site Contamination) Measure (NEPM, 2013) is primarily focused on the standards for assessment of contamination. A number of generic guidance under NEPM will be used in the context of first tier priority contaminants. Further, the NEPM and the National Health and Medical Research Council (NHMRC) provide some criteria for first tier priority contaminants (NHMRC 2013; NHMRC, 2008; NRMMC 2004; ANZECC and ARMCANZ 2000). When assessment criteria were not readily available, CRC CARE incorporated screening levels in its guidance development projects upon recommendation by end-users (Table 1).

The National Remediation Framework (NRF) also developed by CRC CARE includes guidance, which are relevant for remediation of emerging contaminants. Further management and risk-based remediation guidance for first tier priority contaminants are also being developed. It is anticipated that the process of guidance development together with the outcomes will contribute to increased proficiency, efficiency and efficacy in managing contamination for end-users.

Table 1. Guidance being developed for first tier priority contaminants in 2015.

Contaminant	Screening levels	Other guidance
PFOS/PFOA	• Health-based criteria for soil and groundwater • Ecological based criteria for soil, surface water and groundwater • Sediment criteria	• Application of assessment criteria • Risk-based remediation and management guidance
MTBE	• Odour thresholds - groundwater • Groundwater ESLs	• Application of assessment criteria • Risk-based remediation and management guidance
B[a]P	*Soil HILs, GILs, ESLs are already available*	• Application of assessment criteria • Risk-based remediation and management guidance

Stakeholder engagement has been considered through a staged process in guidance development projects by CRC CARE (Figure 1). Technical working groups, consultants and researchers will continue to play a vital role in the development of guidance in these projects.

Figure 1. Generic guidance development process at CRC CARE.

REFERENCES

ANZECC and ARMCANZ 2000, Australian Guidelines for Freshwater and Marine Water Quality, Vol 1 and Vol 2.

CRC CARE 2014a, CRC CARE Technical Report no. 32 Guidance Development for Contaminants of Emerging Concern, CRC CARE Technical Reports, CRC for Contamination Assessment and Remediation of the Environment, Adelaide. Available: <http://www.crccare.com/publications/technical-reports>

CRC CARE 2014b, CRC CARE Technical Report no. 29 Environmental Impact of Priority Contaminants: A Literature Review, CRC CARE Technical Reports, CRC for Contamination Assessment and Remediation of the Environment, Adelaide.

CRC CARE 2013, CRC CARE Technical Report no. 24 Analytical Methods for Priority and Emerging Contaminants – A Literature Review, CRC CARE Technical Reports, CRC for Contamination Assessment and Remediation of the Environment, Adelaide.

NEPM National Environment Protection (Assessment of Site Contamination) Measure, 2013, at <http://www.comlaw.gov.au/Details/F2013C00288>

NHMRC 2008, Guidelines for Managing Risks in Recreational Water, Canberra. http://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh38.pdf

NHMRC 2013, Australian Drinking Water Guidelines, as amended December 2013, National Health and Medical Research Council, Canberra. <http://www.nhmrc.gov.au/guidelines/publications/eh52>

NRMMC 2004, National Water Quality Management Strategy Guidelines for Sewerage Systems: Biosolids Management, Natural Resource Management Ministerial Council, Canberra.

RISK-BASED ASSESSMENT, MANAGEMENT AND REMEDIATION OF PFOS AND PFOA

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INTRODUCTION

Perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonic acid (PFOA) have been identified as contaminants of emerging concern in Australia. They are known to be persistent, bioaccumulative and potentially toxic, and have been found to be present at concentrations of potential concern at a number of sites, particularly where there has been use of fire fighting foams. Industry and public awareness of the presence of particularly PFOS and to a less extent PFOA is growing rapidly, with regular reporting of PFOS contamination in the media, with particular concern being raised regarding the risk that the contamination poses to the health of persons who may be exposed.

In general, there is limited and incomplete information surrounding the occurrence, fate and toxicity of PFCs in the Australian context, and criteria for protecting human health and ecological systems have not been established making it difficult to determine the risk that the contamination poses. Because of the persistence and difficulty of treating PFOS contamination, there is also considerable uncertainty about how such contamination can be treated.

CRC CARE has commenced a project to provide guidance on the assessment, management and remediation of PFOS and PFOA, and has formed a working group comprising representatives of regulatory agencies, industry and research organisations. It is intended that this guidance will assist practitioners, regulators and site owners to effectively assess, manage and remediate soil and groundwater contaminated with PFOS and PFOA, and will allow more appropriate remediation and potentially reduce the cost of managing contaminated soil and groundwater.

It is expected that draft guidance will be prepared later in 2015, and will be circulated for industry review.

In particular, information is being assembled on:

(a) The extent and magnitude of PFC contamination in Australia, where known, and where significant data gaps in knowledge exist;
(b) Ecological and human health screening levels that are available internationally, and which of these, if any, may be appropriate for adoption in Australia;
(c) Impacts on beneficial uses, with a focus on soil, groundwater and receiving waters;
(d) Toxicity, bioaccumulation and persistence; and
(e) The difficulties that arise in treating and managing PFC contamination and reducing the risks to an acceptable level, and practicable approaches that are able to be adopted.

PREPARATION OF GUIDANCE ON THE ASSESSMENT OF PFOS AND PFOA

The presentation will outline the direction of the work, key areas of focus, and a summary of the guidance to date. Key areas are noted in following Table 1.

Table 1. Key areas of focus in the development of Guidelines for PFOS and PFOA

Topic	Current situation	Key gap and focus
Distribution of contamination	Fire training grounds well characterised	Level of contamination in non-fire fighting areas, including landfills, biosolids.
Range of compounds	PFOS and PFOA well characterised	Are PFOS and PFOA the limiting contaminants (compared with other PFCs)
Health based screening levels, including water	Levels are adopted from overseas; reasonably well understood	Determine levels that are consistent with NHMRC and NEPM methodology. Consider bioavailability and bioaccumulation.
Ecological screening levels including water	Levels are adopted from overseas; high degree of uncertainty	Determine levels that are consistent with NEPM and ANZECC methodology Consider bioavailability and bioaccumulation, and potential for exceedance of maximum residue levels in fish.
Sediment screening levels	Levels are adopted from overseas; high level of uncertainty	Determine levels by direct toxicity measurement, concentrations in pore water, and concentrations in the water column
Decision framework	National Remediation Framework being developed by CRC CARE	Adopt approach that is consistent with the NRF
Soil remediation	The requirements for remediation and practical methods of remediation are uncertain.	Apply the screening levels to develop guidance on when remediation is required, and practical methods of remediation and management. Consider ability to reuse low level contaminated soil, containment, stabilisation, treatment. With respect to landfill disposal, identify levels that are consistent with acceptance criteria adopted for similar contaminants.
Groundwater and water remediation	The requirements for treatment and practical methods of disposing of water are uncertain	Apply the screening levels to develop guidance on when clean up is required based on protection of beneficial uses, and advise on practical methods of treatment and disposal. Consider requirements for treatment and discharge treated water to receiving waters, and typical criteria that might allow discharge as trade waste, and the ability to meet these criteria.

RISK-BASED METHODS TO DERIVE AQUATIC ECOSYSTEM GUIDELINES

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INTRODUCTION

The release of the Revised Methodology to derive Australian and New Zealand Water Quality Guideline Values for Toxicants (Warne et al, 2014) and Technical Rationale for changes to the Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants (Batley et al, 2014) represents a significant improvement to development of risk-based guidelines for protection of aquatic ecosystems in Australia. The authors will present their collective experience in developing aquatic guidelines for various toxicants, including development of new perfluorinated chemicals (PFOS and PFOA) guideline values for protection of aquatic ecosystems using the new Warne et al (2014) and Batley et al (2014) methodology. The new Warne et al (2014) and Batley et al, (2014) methodology will be compared to former methods for deriving water quality guidelines, as well as methods for development of screening criteria in other regulatory settings in Australia. The presentation will discuss the following aspects with examples of how differing approaches affect the criteria (numeric value) arrived at:

- Data gathering (literature review)
- Data quality screening (what's in, what's out)
- Data manipulations (Species Sensitivity Distributions versus Assessment Factor approaches)
- Assessment of bioconcentration, bioaccumulation and biomagnification.

Particular focus will be given to the current state of the science in aquatic ecotoxicology testing and the ability to adequately asses and capture adverse chronic effects (such as endocrine disruption, multi-generational effects).

METHODS

The former ANZECC/ARMCANZ (2000) methodology represented a significant development to previous regional or national risk-based methodology for derivation of ecological criteria in Australia and New Zealand. Notably, the advances made in the ANZECC and ARMCANZ (2000) guidance in turn influenced the methodology for derivation of soil ecological investigation and screening levels in the Amended NEPM (1999), although the development of criteria for contaminated land will not be covered except where it highlights an advantage in the revised Australian methodology.

The revised methodology (Warne et al, 2014; Batley et al, 2014) has advanced the scientific rigour and reliability of the risk-based guidelines that may be generated. Some of the key differences between the former and new guidance that will be discussed and include:

- Definition of acute versus chronic tests
- Acceptable test endpoints
- Data selection (acute versus chronic)
- Data conversion (acute converted to chronic, normalising data for the chemical species of interest)
- Testing the data modality
- Improvements to BurrliOz (release of Burrlioz v 2)

RESULTS AND DISCUSSION

The authors' familiarity with risk-based guidance in Australian in three different regulatory settings (national water quality guidelines, chemical hazard classification, chemical risk assessment) will be drawn out in a review of some of the differences and similarities of these respective risk-based methodologies. The authors' experience in screening ecotoxicological data and using these data to derive screening criteria for differing purposes will be presented under the different guidance frameworks. Some of the key differences include:

- Data selection (acute versus chronic)
- Data manipulations (Species Sensitivity Distributions versus Assessment Factor approaches)
- The purpose and application of the screening criterion derived

Examples of how some of these key differences affect the final screening criteria arrived at will be presented. A critical aspect is performing checks and balances performed during appropriate steps and at sufficient frequency to avoid derivation of screening criteria that are potentially over- or under-protective.

CONCLUSIONS

Risk-based guidance frameworks in Australia have improved over the last 20 years and represent international best practice. However, the regulatory setting and applicable methodology to derive a screening criterion, and the ultimate application or purpose of the derived screening criterion can differ significantly under differing regulatory frameworks. The regulatory drivers must be well understood and carefully considered at all stages of data screening, selection, and manipulation. Decisions at each stage of a multi-step process have (sometimes significant) potential to influence the final result. Justifying professional judgements is critical to ensuring transparency and defensibility of risk-based guidelines or screening criteria.

REFERENCES

ANZECC/ARMCANZ (2000). Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. An Introduction to the Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

Batley G.E., R.A. van Dam, M.St.J. Warne, J.C. Chapman, D.R. Fox, C.W. Hickey and J.L. Stauber, Technical Rationale for changes to the Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants, Commonwealth Scientific and Industrial Research Organisation, June 2014

Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW and Stauber JL. 2014. Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants. Department of Science, Information Technology, Innovation and the Arts, Brisbane, Queensland. 36 pp. Batley

ADVANCES IN THE DETERMINATION OF A HUMAN HEALTH SCREENING CRITERIA FOR 6:2 FLUOROTELOMER SULFONATE

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INTRODUCTION

6:2 Fluorotelomer Sulfonate (6:2 FtS) is often detected alongside Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA) in groundwater at contaminated land sites where fire-fighting activities utlising Aqueous Film Forming Foams (AFFF) have been undertaken. While a range of screening criteria are available for PFOS and PFOA in drinking water, a screening criteria for 6:2 FtS in drinking water was unable to be identified from a review of national and international information sources. The chemistry of fluorotelomer based foams is different to that of PFOS/PFOA based foams, suggesting that the toxicity profiles may also differ.

In 2014, a screening criteria of 5.5 µg/L was derived for 6:2 FtS in drinking water (Jarman, Ooi and Hirth, 2014). This screening criterion was based on a review of preliminary dose-response (toxicity) data and was supported by the Threshold of Toxicological Concern (TTC) methodology. The derived value of 5.5 µg/L is an order of magnitude above commonly adopted human health screening criteria for PFOS and PFOA and indicates that 6:2 FtS is less toxic to human health that PFOS or PFOA.

Recently received information has enabled further refinement of the derived screening criteria for 6:2 FtS, and the methodology and results supporting this refinement are presented in this paper.

METHODS

The screening criteria of 5.5 µg/L was reviewed with reference to the following:

(a) Additional algorithms available for predicting toxicity from structural activity relationships (SAR).
(b) Detailed dose-response assessment information obtained for 6:2 FtS.
(c) Toxicity information relating to the bioaccumulation potential for other “C6” chemicals. It is noted that 6:2 FtS has historically been considered to be not bioaccumulative however toxicity information for other “C6” chemicals suggests further consideration is warranted.

In addition, the potential for derivation of a screening criteria for total PFCs using the Toxic Equivalency Factor (TEF) approach is explored.

CONCLUSIONS

The refinement of the screening criterion for 6:2 FtS in drinking water will facilitate decision making at contaminated land site where PFCs are detected in groundwater.

REFERENCES

Jarman, R., Ooi, S., Hirth, D. (2014) *A Human Health Screening Criteria for 6:2 Fluorotelomer Sulfonate (6:2 FtS)*. Proceedings of Ecoforum 2014, Gold Coast, Australia.

DERIVING CRITERIA FOR DIOXINS AND FURANS

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INTRODUCTION

Dioxins and furans are environmental pollutants that are found in mixtures within the environment and have the dubious distinction of belonging to the 'dirty dozen', a group of dangerous chemicals known as persistent organic pollutants (POPs). In the absence of published soil assessment criteria derived by Australian authorities' site-specific risk-based soil criteria (RBSC) were derived to inform and assist in the decision-making process regarding future management options for the site.

The historical manufacture and use of chlorinated phenols over an approximate 20 year period (1951-1975) at a former major hazard facility Site, Melbourne, Victoria, resulted in the generation of dibenzo-p-dioxins and chlorinated dibenzofurans (dioxins and furans) by-products. Dioxin and furans were measured in near-surface soils (0-0.1 mBGL) within former manufacturing areas and in sub-surface soils (0.2-1.0 mBGL) within former effluent treatment settling ponds.

A health risk assessment was undertaken to i) assess the potential health risk of dioxins and furans in soil at the Site and ii) derive site-specific RBSC based on a commercial/industrial setting.

METHODS

The health risk assessment and derivation of site-specific RBSCs was conducted in consideration of the NEPM 2013 (NEPC, 2013). Other Australian guidance (enHealth 2012a and 2012b), the World Health Organisation (WHO) and other international regulatory agencies were also referred to. The risk assessment approach included an evaluation of collected site data using the Toxicity Equivalence Quotient (TEQ) approach (relative to 2,3,7,8-TCDD), published toxicity criteria, exposure assessment, derivation of site-specific criteria and a sensitivity analysis for adopted exposure parameters.

Background exposure was considered by estimating the total dioxin intake from all sources of exposure (i.e. air, food, soil and water) for the Australian adult population of concern as published within the National Dioxins Program (DEH 2004). The information presented in the study presents a lower and upper bound total dioxin intake. Use of the upper bound estimate to represent an exposure intake was considered to be overly conservative (assumes non-detects are the limit of reporting value). Hence, the lower bound total intake of 3.89 pg TEQ/kg/bw/month was adopted in the derivation of the site-specific RBSC. As the majority of the estimated exposure is sourced from food intake, the adoption of the lower bound total intake was considered conservative.

RESULTS AND DISCUSSION

Site-specific RBSCs were calculated for the identified populations of concern: commercial/industrial worker, construction/excavation worker (during construction), construction/excavation worker (post development) and a maintenance/utility worker. The derived site-specific RBSCs are presented in Table 1 together with derived criteria for a different metropolitan site of a similar commercial/industrial land-use setting for comparative purposes.

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Table 1. **Derived Site-specific RBSC.**

Population of Concern	Derived Site-Specific RBSC(1) (µg/kg)	Other Metropolitan Site (µg/kg)
Commercial/Industrial Worker	6.4	35
Construction/Excavation Worker (during construction)	0.45	3
Construction/Excavation Worker (post development)	3.6	-(2)
Maintenance/Utility Worker	22	-(2)

1. Ref: Parsons Brinckerhoff (2014).
2. Denotes criteria not derived for the population of concern.

CONCLUSIONS

A health risk evaluation of measured dioxin and furan concentrations in soil at the Site was undertaken. Site-specific RBSCs were derived and these were accepted by the Victorian EPA-appointed environmental auditor for implementation at the Site under an ongoing commercial/industrial land-use. Deriving site-specific RBSC provided mitigation options in which to manage risks associated with dioxins and furans within a highly complex, industrialised setting.

REFERENCES

Department of Health and Ageing and enHealth Council (2012a) Environmental Health Risk Assessment *Guidelines for assessing human health risks from environmental hazards.*

Department of Health and Ageing and enHealth Council (2012b) *Australian Exposure Factor Handbook*.

Office of Chemical Safety, Australian Government Department of Health and Ageing, 2004, *Human Health Risk Assessment of Dioxins in Australia*, National Dioxins Program Technical Report No. 12, Australian Government Department of the Environment and Heritage, Canberra.

National Environment Protection Council (2013) National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013 (No. 1).

Parsons Brinckerhoff Australia Pty Limited (2014) Health Risk Evaluation – Dioxins and Furans.

REDUCING UNCERTAINITY DURING REMEDIAL DESIGN — A CASE STUDY

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INTRODUCTION

Thiess was engaged to remediate a former service station site in Perth, Western Australia. Contamination at the site originated from the former underground petroleum storage system (UPSS), and was present in the unsaturated and saturated zones. The geology primarily comprised interbedded sandy-, silty-clay with a range of permeabilities. The groundwater table was located at approximately 6 metres below ground level.

Excavation and disposal of soil to landfill was the selected remediation strategy for unsaturated zone soil. Solvent enhanced insitu chemical oxidation (SE-ISCO) was the selected remediation strategy for saturated zone soil and groundwater.

REDUCING QUANTITY UNCERTAINITY

Multiple methods were used to reduce quantity uncertainty during the remediation planning phase. The techniques included:

(a) High Resolution Site Characterisation using a membrane interface probe (MIP) / laser induced fluorescence (LIF) survey;
(b) Laboratory treatment trials to optimise remediation technologies;
(c) 3D modelling of the geology, above ground features and the distribution of contaminants; and
(d) A Construction Hazard Assessment Implication Review (CHAIR) process for the proposed remediation methods.

High Resolution Site Characterisation

A MIP/LIF survey was conducted at the site. The survey provided data that was used to generate a 3D model of the contamination at the site. The survey identified that contamination in the unsaturated zone was more widespread than previously thought. As a result a change in methodology to the shallow excavation was developed. During the subsequent excavation, still more contaminated soil not identified by the MIP/LIF survey was found.

Treatability Trials

Laboratory treatability trials were undertaken to optimise the groundwater remediation design. The trials identified the required mass and concentration of the co-solvent, oxidant (sodium persulphate) and activator (sodium hydroxide).

3D Modelling

The remediation volume specification for the site had a high degree of uncertainty, due to the complex geology and limited extent of available investigation data. The approach at this site was to cost-effectively reduce the remediation volume uncertainty by undertaking additional high resolution investigation and generating 3D contaminant distribution models for a number of remediation strategies. The models incorporated:

- The extent of contamination identified by the MIP/LIF survey;
- The location of known utilities and the UPSS;
- Features of the remediation strategy such as excavation support systems;
- The location of monitoring and remediation wells; and

- The location of above ground features such as buildings fencing, trees, entrances / exits, and excavations.

CHAIR Process

Remediation strategies were tested using a team of personnel with varying expertise, including safety, design, engineering, project management and implementation. In addition other project stakeholders were consulted to create a mutually-equitable solution.

RESULT

The process teased out a range of issues for each remediation strategy that could be dealt with in the remediation planning phase prior to commencing site works. The final remediation approach developed by the design team, took into account the location of above ground and below ground infrastructure. The finished remediation design model was a virtual graphic tool that allowed the design team to understand physical constraints and opportunities for the site remediation.

REFERENCES

WorkCover (2001) *CHAIR, Safety in Design Tool*

USING MASS BALANCE IN RISK ASSESSMENT

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INTRODUCTION

Quantitative risk assessments are often conducted with constant steady state source concentrations and an unlimited mass available for potential exposures. For many exposure scenarios and available site data these conservative assumptions are appropriate and can be useful when data are available to understand the limits of mass. Accounting for mass balance minimises the unnecessary conservatism in risk assessments. The National Environment Protection Measure (NEPM, 1999) has already adopted this approach in in the 2013 updated inclusion of the soil Health Screening Levels (HSLs). In developing the soil HSLs protective of vapour intrusion, a finite source model was used to reduce the disparity in finite vs. infinite source modelling from typical residual soil impacts (Friebel and Nadebaum, 2011). An evaluation of a finite mass balance vs. infinite source approach was applied to vapour intrusion assessment for a scenario of petroleum hydrocarbon impacted groundwater seepage into a car park basement. This provided an example where simple mass balance evaluation can refine the risk assessment process and reduce the conservatism.

METHODS

There are several model options available to estimate the vapour emissions from seepage water, each based on different assumptions regarding the primary mechanisms controlling vapour migration (CRC Care, 2013). Some models are based on standing pools of water and others are based on models developed for flowing water bodies such as rivers. Both of these models assume an infinite source. These approaches also rely on parameters such as water velocities, wind velocities and seepage crack areas which are not easily measured.

Both modelling approaches were used to develop site-specific target levels for vapour inhalation associated with petroleum hydrocarbon impacted groundwater seepage into a car park basement, and to support remediation planning. The sensitivity of this model selection and consideration of mass balance is evaluated here. To evaluate the mass balance approach an understanding of total volume water flux was taken from the average water recovery rate from an existing groundwater extraction system.

RESULTS AND DISCUSSION

The results show that for benzene the estimated mass flux from the mass limited model was an order of magnitude lower using infinite source flux modelling. The mass balance method is also conservative as it assumes that 100% of the benzene mass that may be in groundwater could seep into or migrate under the slab of the basement volatilises into the basement air and is available for exposure.

CONCLUSIONS

Also, the results of the mass balance comparisons provided a limit to the sensitivity of the modelling approach to parameters that are difficult to measure (e.g. water velocities, wind velocities and seepage crack areas). Thus the application of the mass balance eliminated focus on understanding these parameters and using overly conservative inputs. Ultimately, the results provided a quantitative evaluation of the uncertainties in the risk assessment and provided confidence that the risk assessment was unlikely to underestimate risk.

REFERENCES

CRC CARE 2013, Petroleum hydrocarbon vapour intrusion assessment: Australian guidance, CRC CARE Technical Report no. 23, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Friebel, E & Nadebaum, P 2011, ‘Health screening levels for petroleum hydrocarbons in soil and groundwater. Part 1: Technical development document’, CRC for Contamination Assessment and Remediation of the Environment, CRC CARE Technical Report no. 10, Adelaide.

National Environment Protection (Assessment of Site Contamination) Measure (NEPM). 1999. As updated per the Amendment Measure 2013 (No. 1). National Environment Protection Council.

FAST TRACKED — THE ENVIRONMENTAL RISKS AND CHALLENGES OF GRADE SEPARATION PROJECTS

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INTRODUCTION

In recent times, grade separation projects have gained attention from various stakeholders in the infrastructure, engineering and environmental sectors across Victoria and Australia. Unlike other recent infrastructure projects, there is a broader community support and consensus on the benefits associated with grade separation projects, which also bring additional opportunities for improvement/rebuilding of existing stations, construction of car parks and targeted development.

However, delivery of these projects is not free of logistical, engineering and environmental challenges which are uniquely associated with the setting, scale and the time constrains of the each grade separation.

This study presents an overview of the main risks and challenges associated with grade separations with respect to land contamination and groundwater with the aim of raising awareness amongst stakeholders on potential issues to be considered and faced during procurement, design and construction.

LAND CONTAMINATION

The majority of grade separations are likely to be realized by excavation of a tunnel to separate road and rail traffic, with the ‘rail under’ option generally preferred to the ‘road under’ option. Depending on logistical constrains, the works can be realized ‘in-line’, with temporary interruption of the train services, or ‘off-line’, where a temporary line diversion is in place to guarantee continuity of services.

For an environmental perspective, there are various issues to consider with respect to soil excavation works, comprising:

- Presence of contaminated fill above natural soils, which could be present with various extent along the rail line (i.e. under the ballast), in rail embankments and at train stations.
- Contaminated ballast, resulting from ongoing minor spills and losses of hydrocarbon fuels and lubricating oils from trains and from asbestos associated with brake pads.
- Contaminated soil associated with historical/current industrial land uses, landfilling and electrical substations in proximity or within the rail corridors and the train stations.
- Excavation and disturbance of actual or potential acid sulfate soils.

Considering the extremely compressed timelines of the ‘in-line’ solutions (ranging from four to six weeks) and the limited opportunities to stockpile large volumes of potentially contaminated soil within the site during the works, it is paramount that appropriate assessment of soil contamination issues is undertaken at the planning and design stage of the excavation.

The soil investigation works, which can be targeted following preliminary desktop review of potential sources of contamination, should be designed to allow the project team to make informed estimates and decision of the following:

- Volumes, type and category of contaminated materials produced by the excavation
- Risks to construction workers

- Opportunities for on-site reuse or disposal of excavated materials
- Characterisation and management of acid sulfate soils.

GROUNDWATER

It is not unusual for portions of the grade separations structures (i.e. rail tunnel, stations) to be below the average level of the groundwater table for significant extents.

When this is the case, groundwater dewatering is likely to be required during construction to allow for dry conditions at the base of excavation. In addition, depending on the final design of the structures below the water table (drained or impermeable), dewatering may be required during the entire design life of the project. The main implications associated with groundwater dewatering are summarised below:

- Estimate of groundwater inflows to allow for sizing of the construction and permanent (in case of drained structure) dewatering systems.
- Assessment of sustainability of long term drained solutions, which are usually less expensive in terms of capital costs compared to impermeable solution but have ongoing legacy issues associated with management of groundwater.
- Groundwater quality and potential for the 'cone of depression' associated with dewatering to mobilise nearby groundwater plumes.
- Ability to dispose of dewatering volumes to sewer or other receptors and water treatment requirements prior to disposal.
- Effects potentially associated with groundwater drawdown with respect to ground settlement, generation of acid sulfate soils, groundwater dependant ecosystems and groundwater users.
- Vapour risks to workers and long term users of the structures in case of groundwater contaminated by volatile compounds.

Similar to land contamination, groundwater issues should be thoroughly addressed at the early stage of the project to allow for adequate assessment of risks and development of management measures to be adopted during and post construction. Typically, this would require an integrated approach combining groundwater quality investigations, hydraulic testing and groundwater numerical modelling to provide the required inputs to the design team as the project progresses from design to construction and operation.

CONCLUSIONS

Grade separations have the ambition to ease congestion, improve public transport and increase safety in our cities. This study has identified the main land contamination and groundwater challenges faces by these types of infrastructure project, which are considered significant in light of the nature of these types of project and the tight timelines for delivery.

It is considered that early planning supported by adequate investigation is a key element for the successful delivery of the project, allowing to make informed decisions on management of excavated materials, control of groundwater during construction and more sustainable design solutions.

OCCUPATIONAL HYGIENE IN THE REMEDIATION INDUSTRY: A REVIEW OF RISK IN RECENT CASE STUDIES DURING GASWORKS REMEDIATION

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BACKGROUND

The remediation industry brings with it many unique hazards, which relies on competent advice to control occupational exposure to the various chemicals of concern.

The qualitative determination of occupational health risk is an important step to anticipate the control measures needed to reduce occupational exposure prior to remediation activities commencing. Such a risk assessment is then strengthened through the collection of quantitative data during the overall remediation process.

METHODS

This paper will take a retrospective look back at the overall effectiveness of this risk assessment process to control occupational health risk on two recent gasworks remediation projects.

It will discuss the process involved in establishing such a risk assessment program inclusive of basic characterisation of environmental agents, the remediation process, the chemicals of concern, and the overall scope. It will focus on the process of defining Similarly Exposed Groups (SEGs) and the associated design of control measures needed to reduce occupational exposure.

Whilst controlling occupational exposure to any hazard remains the most important task, monitoring is often necessary to determine the effectiveness of those controls, and to demonstrate compliance with regulatory requirements. A review of such monitoring data will be presented to demonstrate the advantages to this overall process.

RESULTS AND DISCUSSION

This paper will step through the process undertaken on gasworks remediation projects to manage occupational health during contaminated works. Personal exposure data obtained from within the remediation area will be presented to demonstrate the effectiveness of the control measures in place for worker health.

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ASSESSING CONTAMINATED SITES DATA — TRADING ACCURACY FOR KNOWLEDGE

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INTRODUCTION

Current practice in characterising of contaminated sites focuses on demonstrating accuracy of the analytical information generated through Data Quality Indicators (DQI's) and relies on assumptions with regard to the representativeness of the data in the real world. Another peculiarity when generating data for contaminated sites is the limitation imposed by not homogenising samples to prevent loss of volatiles.

Alternatives to the current approach trades some of the perceived accuracy of the information for a more comprehensive understanding of the 'real' rather than assumed bulk soil characteristics for a similar cost of investigation.

CURRENT APPROACH AND LIMITATIONS

Current soil analysis methods place a heavy emphasis on the accuracy of the laboratory data without necessarily considering the Representative Elementary Volume (REV). Hill (1963) defines the REV as the smallest volume over which a measurement can be made that will yield a value representative of the whole. This focus on accuracy can lead to a loss of perspective with respect to soil bulk characteristics and an overreliance on assumptions as to what the laboratory result mean in the real world. The US EPA notes that the relative contribution to decision error in contaminated land characterisation in order of significance are:

In general practice the effort spent on understanding each of these contributors is almost reversed, leading to a heavy reliance in assumptions on REV that are often not applicable to the true soil bulk characteristics of the site.

ALTERNATIVES

Traditional contaminated site characterisation has some significant limitations that can lead to significant decision errors. These can result in a range of future problems such as liability remaining, remediation cost overruns or unnecessary expenditure on remediation and time delays that cost money, waste resources and impact the environment.

The US EPA triad approach was the first significant attempt to remedy the limitations of the traditional site characterisation process (Environmental Agency 2009). Since inception, the process has evolved and focuses on trading some accuracy in the concentration measurement for more data of lower perceived accuracy to improve understanding of the REV at similar or lower cost. This approach uses a combination of field techniques coupled with spatial geo-statistics to achieve a significant improvement in the understanding and reliability of REV and site characterisation.

Sample Scale

Field portable instruments such as X-ray Refraction Analysers (XRF) allow rapid real time collection of inorganic analyte data in the field and can significantly improve understanding of both intra- and inter-sample variability. Data from several investigations demonstrate the potential flaws in the current approach of accurately measuring concentration in a very small sub-sample and assuming it is representative over an assumed volume, particularly when this assumed volume is many orders of magnitude larger than the volume used in the laboratory analysis.

A recent project analysed more than 450 soil samples for lead concentration in the laboratory. These samples were also subject to 5 analysis with an XRF. Table 1 presents selected results (based on measured concentration range) of that data, which had an R^2 of 0.89 between the laboratory and XRF measured lead concentrations.

Table 1. Selected Pb Results (Single Laboratory vs 5 Individual Readings same XRF).

Laboratory mg/kg	XRF 1 mg/kg	XRF 2 mg/kg	XRF 3 mg/kg	XRF 4 mg/kg	XRF 5 mg/kg	RPD(%) XRF
150	136	190	206	153	170	20%
300	155	526	161	400	242	54%
540	2668	360	374	402	374	76%
2000	1440	3877	2150	5696	2414	60%
18000	19600	30706	30627	20624	20949	22%
29000	18884	28296	18865	19908	26033	20%

The results demonstrate the benefit of using multiple measurements of a sample using a method that trades some accuracy and repeatability for speed to provide a better overall characterisation of lead concentration in the soils. The results demonstrate that the volume of soil used in the laboratory analysis may not adequately represent the REV (heterogeneity) and increases decision error risk.

Site Scale

Kriging-based bi-variant statistics used in the mining industry offers an alternative to the classical approach to interpreting spatial distribution and offers the key benefit of linking concentration and location. This approach provides an improved means of interpolation of the concentration data across a site. This paper demonstrates the use of an integrated bi-variant statistical approach that includes the location, primary data and QA/QC data to provide decision makers improved information and greater understanding of potential uncertainties in contaminant distribution.

The variogram required to facilitate kriging is based on the total data set and utilises all measurements, including the multiple QA measurements collected for each sample. Use of the total data set improved the representativeness of the variogram with respect to the random variance component (sample scale variance). The final step used indicator kriging using a probabilistic approach that allows integration of measurement uncertainty into the spatial geostatistical process. This allows incorporation of all potential sources of concentration variability and sample scale decision uncertainty into one process to improve understanding of the reliability of the site characterisation.

CONCLUSIONS

Trading some accuracy in concentration measurement for quantity of analysis to better understand the REV and utilising this data in a spatial geo-statistical assessment, provides an integrated approach to improved site characterisation and understanding of uncertainty. The REV concept focuses improving understanding the representativeness of the concentration measurement on the sample scale.

Using the total concentration data set in the spatial geo-statistical assessments that considers decision uncertainty further improves understanding of characterisation on the site scale.

REFERENCES

Hill. (1963) Elastic Properties of Reinforced Solids. *J.Mech.Phys.Solids*. Vol 11. 357-372.

Environmental Agency. (2009) Framework for the use of rapid measurement techniques (RMT) in the risk management of land contamination. *Environment Agency – March 2009*.

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GROUND GAS RISK MANAGEMENT — LESSONS LEARNT FROM AN AUDITOR’S PERSPECTIVE

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INTRODUCTION

Australia is littered with former landfill sites, many of which are gas producing and not formally engineered. As increasing urban growth pressure makes more these sites economically viable to develop, former landfills can become attractive to the property market. As part of the subsequent development, contaminated site Auditors are being required to review site assessments and remedial options for these sites, as well as to certify the actual implementation of remedial measures. The potential risks posed by landfill sites are numerous and include ground gas, leachate and subsidence. Ground gas from landfills poses a potential acute risk to surrounding properties as well as the site development, which is in contrast to the majority of contaminated land risks and is often poorly understood by developers and consultants alike.

Excavation and disposal of the landfill material is prohibitively expensive and technically impractical so in-situ remediation and management methods are required at these sites. Prior to determining the most applicable method for controlling the risks posed by an individual site, it is vital to ensure that the site subsurface is adequately understood. Similarly, design of pilot trials of proposed methodologies is vital to the success of ongoing site management.

METHODS

The assessment of risks posed by, and potential resolutions for, landfill gas at former landfill sites is examined through two case studies – one involving a proposal for residential development in close proximity to a former “inert” landfill, and one involving commercial development. Both projects are ongoing. The second has progressed to pilot trials of active and passive technologies for gas management.

RESULTS AND DISCUSSION

Education of clients regarding the seriousness of the potential risks and implications for proposed developments is essential, as these factors can be expensive and time consuming. Whilst most consultants recognise the potential risks posed by landfill gas, not all have a thorough understanding of the practicalities of thorough site assessment and the detailed design and pilot testing of potential remedial methods. From the Auditor’s perspective, thorough scientific documentation of proposed remediation/management systems is required, along with an appreciation of the engineering and cost implications of any recommended remediation or management measures.

INSTALLATION AND PILOT TRIAL OF SOIL VAPOUR EXTRACTION (SVE) FROM A HORIZONTAL WELL IN THE NEWER VOLCANICS BASALT BENEATH AND OPERATING PLANT BUILDING

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INTRODUCTION

Remediation of a petroleum hydrocarbon plume in the fractured basalt of the Newer Volcanics beneath an operating plant building, owned and occupied by other parties, represented a unique set of challenges. Due to the significant logistical constrain on the use of conventional vertical remediation wells, directional drilling methods were used to install a horizontal well, with a 243 m long screened section, over the axis of the plume was trialled.

BACKGROUND AND OBJECTIVES

A petroleum hydrocarbon plume associated with releases of both petrol and diesel from former underground storage tanks (USTs) extended diagonally beneath a plant building and across the site boundary hydraulically down-gradient. The secondary source area with the plume, where residual light non-aqueous phase liquids (LNAPL) were believed to be present, was approximately 250 m in length and was almost completely covered by the plant building. The dissolved phase portion of the plume extended approximately 150 m further hydraulically down-gradient.

Based on precedence with similar groundwater impacts on other sites, achieving regulatory ‘closure’ through a CUTEP determination was unlikely without some significant attempt to reduce the mass of residual LNAPL in the plume. A Remediation Feasibility Assessment identified SVE via horizontal wells as potentially the most practicable approach to remediation of the plume. Air sparging and SVE moving to biosparging were also identified as potentially feasible options, if it could be demonstrated that SVE could effectively manage risk of fugitive emissions from migrating into the overlying plant building.

Although used extensively internationally and in other formations in Australia, horizontal wells had not been used for remediation purposes in the basalt to date. The objectives of the trial included the following:

- Assess the constructability and cost of the horizontal well.
- Assess the effectiveness of horizontal well to achieve a significant vapour flow rate and mass removal.
- Assess the potential effectiveness of the SVE to contain fugitive emissions from sparging.

METHODS

Senversa contracted Australian-based directional drillers that had experience in drilling and installation of underground infrastructure in the basalt and fractured rock. Dr George Losonsky, an internationally recognised expert in horizontal remediation wells, developed designs and processes to address the key areas that local contractors would not have previously addressed. Well development and design of the well slot spacing to maintain an approximately even vacuum along the relatively long screen length. Dr Losonsky also played a key role decision making during installation and testing of the well.

A 150 mm diameter, 375 m long pilot hole was directionally drilled and back-reamed out to 360 mm diameter. A 150 mm diameter HDPE pipe was fabricated with a 243 m long screened section and then drawn into the borehole. SVE testing of the well was conducted over a week along with monitoring of volatile organic chemical (VOC) concentrations in

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extracted vapour and 15 surrounding vertical monitoring wells. An additional short term SVE trial was conducted on an existing remediation system in a separate petroleum hydrocarbon plume at the site to compare performance of vertical and horizontal remediation wells in the Newer Volcanics basalt.

RESULTS AND DISCUSSION

Construction issues included avoiding “frac-out” of drilling fluids into the plant building, accurately ‘steering’ the drill bit within a design depth interval above the water table and well development. These issues were effectively managed using a range of methods.

The average vapour flow rate from the horizontal well was 525 m^3/hour under a vacuum of -37 kPa. Vapour flow rate per metre of well screen from the horizontal well in the basalt were between approximately 50% to an order of magnitude less than flow rates per m of screen measured from horizontal wells in a range of projects internationally, indicating that the basalt at the site is at the low end of effective porosity in which vapour extraction is practicable. However, the vapour flow rate per metre of screen from the horizontal well compared very favourably to measured flow rate per metre of screen from vertical wells at the site, being approximately 1.4 to 4.6 times higher than vertical wells.

The concentrations of VOCs in the vapour extracted from the horizontal well were relatively low and generally consistent with VOC concentrations measured in vertical monitoring wells around the horizontal well. Relative consistency between VOC concentrations in the horizontal well and vertical wells suggests SVE from a well above rather than intersecting the water table is not a critical issue.

Despite a reasonable vapour flow rate (525 m^3/hour), low VOC concentrations resulted in a low predicted mass removal rate for full-scale implementation (100 kg/year to 500 kg/year). Results high-lighted the need to obtain reliable measured vapour flow rates and use of laboratory determined TRH C_6 to C_9 to assess mass removal rates, a key indicator of effectiveness and practicability. Laboratory determined VOCs in vertical monitoring wells may be a feasible key indicator of practicability of SVE in the basalt.

No vacuum was measured in any of the vertical monitoring wells surrounding the horizontal well during the SVE trial, high-lighting the heterogeneity of fractures in the basalt and poor hydraulic connection between fracture systems. Based on these results, SVE from the horizontal well will not provide a reliable means of managing fugitive emissions from a potential sparging system from entering the overlying plant building. Monitoring of respiration parameters in surrounding monitoring wells suggested that SVE may induce diffusive processes in the surrounding formation.

Comparison of costs for installation per metre of well screen for a horizontal well ($1,975) compared to an equivalent vertical well system ($1,375) are higher, but may be off-set by the improved effectiveness in vapour flow rates per metre.

CONCLUSIONS

Remediation of this particular petroleum hydrocarbon plume is not considered practicable due the low VOC concentrations in the vadose zone over the plume. However, if sufficient VOCs are present in vapour, SVE via a horizontal well may achieve meaningful mass removal rates. Remediation involving sparging is not considered practicable in the basalt beneath a sensitive receptor on the basis that potential fugitive emissions cannot be reliably controlled.

Horizontal remediation wells are a realistic option in the basalt and likely to be more effective in vapour extraction from the basalt than conventional vertical wells. The higher cost of horizontal wells is likely to be off-set by improved effectiveness in achieving vapour flow.

ASSESSING THE HYDROCARBON NATURAL SOURCE ZONE DEPLETION RATE OF NON-AQUEOUS PHASE HYDROCARBONS BY MEASURING SOIL GAS FLUX

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INTRODUCTION

Cardno Lane Piper (Cardno) undertook an assessment of the Natural Source Zone Depletion (NSZD) rate of Non-Aqueous Phase Liquid (NAPL) in the unsaturated zone at two former fuel depot sites in Victoria. NSZD is the biodegradation of NAPL in the groundwater and vadose zone. The study assessed the NSZD rate of NAPL by measuring soil gas flux using E-Flux carbon dioxide (CO_2) traps (provided by E-Flux, LLC). CO_2 is produced by microorganisms as a by-product of the biodegradation of NAPL which diffuses to the surface and is collected in the E-flux traps by conversion of calcium hydroxide to calcium carbonate (McCoy, *et. al*., 2014). Background CO_2 flux measurements allows the subtraction of background flux, and carbon isotope analysis allows the subtraction of CO_2 generated by natural soil respiration (such as the breakdown of organic matter), in order to determine the fossil fuel carbon fractions of the sorbed CO_2 (Zimbron *et. Al.*, 2011). Finally, the quantity of sorbed CO_2 is converted to the NSZD rate of NAPL (in mass/area/time) using an appropriate stoichiometric ratio between CO_2 and NAPL.

METHODS

The study was conducted at two sites from May to December 2014. CO_2 traps were at the site surface and left for approximately two weeks. The traps were then collected and analysed by a laboratory. A previous Laser Induced Fluorescence (LIF) investigation at Site 1 identified three contaminant zones (depth and location): deep impact (>4m), shallow impact (<4m), and an area containing both shallow and deep impact. Nine CO_2 traps were placed above the three identified contaminant zones. For Site 2, six traps were installed at targeted locations within the impacted area (groundwater benzene concentration >5,000 µg/L). One background trap was also installed at each site.

RESULTS AND DISCUSSION

The average NSZD rate for each site is presented in Table 1.

Table 1. NSZD rate of NAPL within target zones at each site.

Site No.	Target NAPL Zone	Area (ha)	Average NSZD rate of NAPL		
			L/ha/year	kg/year	kg/day
Site 1	Shallow & Deep Zone	0.13	9433	1004	2.75
	Deep Zone	0.29	1627	312	0.85
	Shallow Zone	0.13	7805	830	2.27
	Total			1142	3.12
Site 2	Benzene >5,000 µg/L Zone	0.33	428	113	0.31

NSZD rate of NAPL at Site 1 calculated from the traps targeting deeper contamination was approximately one fifth of that calculated for the shallower contamination, attributed to:

- There is likely to be less oxygen available deeper in the soil profile;
- The deeper impacts are often below the groundwater SWL (i.e. trapped NAPL). Groundwater is likely to limit the oxygen flux to the NAPL in the deeper impacts;
- A greater depth or sectional area of impacted soils being available for NSZD in areas of the site where there is shallow and deep impact.

At Site 2, the NSZD rate of the trap targeting NAPL was approximately three times higher than the traps targeting dissolved phase areas only.

Table 2. Hydrocarbon mass recovery rates from active remediation.

Site 1 (on-site system, air sparge/SVE)		Site 2 (Mobile MPE)	
Remediation Period	Mass Recovery Rate (kg/year)	Remediation Period	Mass Recovery Rate (kg/day)
First year of operation	1,012	2011	0.45 - 6.32
Second year of operation	17	2012	0.55
Third year of operation	2	2014	0.94 - 3.79

At Site 1, NSZD removed 1,142 kg/year, approximately the same mass of hydrocarbons as was removed by the remediation system in its first year of operation. In subsequent years, the NSZD rate is far in excess of the rate of hydrocarbon removal achieved by the remediation system. The greenhouse gas emissions generated by energy use by the remediation system is estimated to be approximately 77,000 kg/year. At Site 2, the average NSZD rate of NAPL (0.31 kg/day) is an order of magnitude less than the average hydrocarbon mass recovery rate achieved in the past by short term MPE events. MPE mass removal rates have varied significantly between events, and may be able to be increased with the installation of additional extraction bores. It is noted that MPE is an energy and cost intensive process, using over 10L of diesel per hour of operation, equating to approximately 26 kg of CO_2 per hour.

The approximate mass of NAPL present in the vadose zone of Site 1 was calculated using a method adopted from Kuo, J. (1999) and subsequently used to estimate the time required for site remediation by NSZD; results are shown in Table 3. There was insufficient data to approximate the mass of NAPL remaining at Site 2. Given the uncertainty in the calculations, it is appropriate to use this estimation as evidence that if the site were remediated by NSZD alone, then NAPL depletion would occur over decades, rather than years or centenaries.

Table 3. Estimated mass of NAPL remaining at Site 1 and estimated remedial time via NSZD.

Target NAPL Zone	NSZD rate (kg/year)	Estimated mass of NAPL remaining (tonnes)	Estimated Remedial Time via NSZD (years)
Shallow Zone	830	10	12
Deep Zone	312	5.8	19

CONCLUSIONS

This paper provides an assessment of the NSZD rate of NAPL at two sites calculated from CO_2 mass flux. More generally:

a) The NSZD rate can be simply and cost effectively measured by CO_2 traps and subsequently compared to hydrocarbon removal rates using active remediation or be used to estimate site remediation time by NSZD;

b) NSZD assessment, using CO_2 traps and other tools, is considered a useful approach for providing substantiated lines of evidence for determining the practical limits of active remediation (e.g. when NSZD significantly exceeds active NAPL removal rates) and for achievement of remediation end points, like removal of NAPL to the extent practicable, if combined with other metrics (e.g. LNAPL transmissivity).

c) NSZD (including MNA in the saturated zone) is a viable remediation or management strategy at some sites where some NAPL remains. Assessment using CO_2 traps provides substantially more accurate information on the rate and success of NSZD/MNA than a traditional MNA assessment using groundwater concentrations;

d) NSZD, which evolved from a revised LNAPL Conceptual Site Model science, can be used as part of remediation options and feasibility assessments, which need to include aside from technical, logistical and financial considerations an integration of life cycle analysis and intergenerational equity of remediation efforts.

THE USE OF PASSIVE SOIL GAS (PSG) SURVEYS TO IMRPOVE THE USABILITY OF INFORMATION GATHERED DURING PRELIMINARY SITE INVESTIGATIONS AT PETROLEUM CONTAMINATED SITES

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INTRODUCTION

Contaminated site assessments were required for fifty six (56) fuel service station sites and two (2) bunkering facilities in Jamaica. The assessments sought to determine the environmental status of facilities to be included in a proposed fuels business asset purchase. The primary constraint of the project was time as the information had to be obtained in six (6) weeks in order to make key decisions regarding the asset purchase. The key objectives were to identify the extent of contamination at the sites and provide information to develop detailed site investigations and remediation plans.

Preliminary site investigations (PSI) were undertaken in conjunction with passive soil gas (PSG) surveys as this would provide information in far less time than typical drilling/active soil gas measurements. The data obtained allowed the identification of the most at risk sites and the extent of contamination present at all sites. The surveys were conducted using PSG samplers installed in sub-surface soils which adsorbed volatile and semi-volatile organic compounds (VOCs and SVOCs) in soil gas. The samplers were deployed in a grid, facilitating the simultaneous sampling of trace levels of soil gas compounds sourced from contamination in soil or groundwater. The concurrent sampling of on-site locations normalised the temporal variations in soil-gas concentrations that typically occur. The spatial variability of contamination was better defined because the lower sampling and analytical costs of the method allowed for more locations to be sampled when compared with traditional intrusive active sampling methods. The method did not alter the natural flow rate of gas, yielding a more representative sample than active soil gas techniques.

METHODS

PSG samplers from Beacon Environmental were used to collect soil gas and were deployed in a grid across the sites. To install the sampler, an approximately four (4) cm diameter hole was drilled through the surfacing to the underlying soils and a 2.5cm diameter hole was then advanced to approximately one (1) metre. The PSG sampler (which contains two sets of hydrophobic adsorbent cartridges) was installed in the hole, which was then sealed with an aluminium foil plug and a thin concrete patch to protect the sampler from external vapour and moisture intrusion. The samplers were left in place for seven (7) – ten (10) days with a length of wire wrapped around the vial and twisted around the shoulder of the vial to expedite retrieval from the ground. Following the exposure period, the samplers were retrieved and shipped to Beacon Environmental for analysis.

Soil gas samples were analysed using thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrumentation, following modified EPA Method 8260C procedures. Samples were analysed for a list of forty-nine (49) compounds, including total petroleum hydrocarbons (TPH). Isopleth maps were prepared for masses of selected contaminants of concern (COC). Maps were prepared for (a) Total BTEXN, which is the sum of the results measured for Benzene, Toluene, Ethylbenzene, Xylenes and Naphthalene; (b) Total Trimethylbenzenes (sum of 1,3,5-Trimethylbenzene and 1,2,4-Trimethylbenzene); and (c) Total Petroleum Hydrocarbons (sum of TPH C5-C9 and TPH C10-C15). These compounds were chosen based on their toxicity and/or mobility in soil and groundwater. The analytical results were reported in units of mass allowing comparison between sample locations to identify source areas and to delineate the lateral extent of contamination.

RESULTS AND DISCUSSION

Fuel Bunkering and Storage Depot

(a) The contaminant distribution was found to be highly localized and there were distinct hotspots identified for Total BTEXN, Total Trimethylbenzenes and Total Petroleum Hydrocarbons. One hotspot was found to correlate with the location of a previous leak reported from a Toluene tank on-site; and

(b) The TPH hotspots identified in the PSG data was used to guide groundwater sampling. The concentration of TPH in the groundwater sampled within the hotspot zones were found to be greater than those sampled from bores placed without the use of the PSG data. This highlighted the utility of the PSG surveys for the determination of groundwater bore locations.

Service Station Sites

PSG data was collected at both active and abandoned service stations and their contamination statuses determined. The results are summarised as follows:

(a) PSG mapping allowed the identification of potentially significant sub-surface contamination at a number of the service station sites assessed;

(b) Combined with current and historical site information, the ability to identify contaminant sources was improved;

(c) These data in conjunction with the information of the volatility of compounds, depth to groundwater, mobility in soil and groundwater, levels of toxicity and proximity to environmentally sensitive sites allowed the determination of environmental risk for each site assessed; and

(d) Relative risk of contamination was determined and risk rankings established.

CONCLUSIONS

The results of these assessments show the utility of PSG surveys in the determination of sub-surface VOC and SVOC contamination. The ability to map and overlay the distributions of soil-gas compounds with the critical services on site (tanks, piping, bowsers etc.) facilitated the identification of potential problem areas and sources of contamination. The PSG surveys were shown to enhance the ability to locate areas of elevated TPH concentrations in groundwater and guide the location of groundwater bores. It has been shown that the implementation of the PSG methodology in conjunction with the data collected during the PSI (site history, layout, spill and contamination history etc.) allowed the assessment of all sites within the constraints of time defined by the project and enabled the undertaking of semi-quantitative risk assessments and the assignment of risk rankings to identify the most at risk sites. The enhanced value of information gathered facilitated improved decision making regarding detailed site investigations and remediation options.

REFERENCES

ASTM Standards (2011) *D7758-11, Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations*, West Conshohocken, PA, 2011: ASTM International.

USEPA (2006) *Method 8260C (SW-846): Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3*. http://www.epa.gov/sam/pdfs/EPA-8260c.pdf .

AN INTEGRATED INVESTIGATION APPROACH FOR CHARACTERISATION OF A LANDFILL LEACHATE PLUME

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INTRODUCTION

A high-resolution investigation was performed to characterise the variability in landfill leachate discharge and migration in groundwater down hydraulic gradient from an old, unlined landfill in South Sydney (Astrolabe Park), NSW. The former landfill consisted of disposal of municipal waste into a former sand mine pit, with a portion of the waste extending below the water table. The landfill was situated in a portion of the Botany Sands Aquifer, consisting of a shallow sandy aquifer with local groundwater flow and discharge into a pond a short distance downgradient from the landfill (Jorstad, 2006; Jorstad et al, 2003)..

An integrated approach to field investigation was utilised, including detailed characterisation of groundwater chemistry using a network of standard monitoring wells and bundled piezometers, and surface and borehole geophysical investigation techniques.

METHODS

Various complementary investigation techniques were employed during the study, including:

a) Multi-level piezometers were installed to provide detailed vertical groundwater chemistry profiles. Sampling points were installed at 0.5 to 1 m vertical spacings, and were used for field measurement of leachate indicator parameters and collection of groundwater samples for laboratory analysis.
b) Hydraulic head values were measured in the multi-level piezometers using a novel ‘manometer board’ method (Acworth et al, 2007), to provide high resolution vertical head profiles;
c) Borehole geophysical methods, including bulk electrical conductivity and gamma emission logs, were used to provide high resolution vertical characterisation of the electrical anomaly created by the leachate plume, and to identify fine-grained lenses within the sandy aquifer profile (Acworth and Jorstad, 2006);
d) Surface resistivity measurements were performed to assess the bulk electrical properties of the aquifer along transects between the landfill and a downgradient pond. The surface resistivity transects provided a two-dimensional electrical image of the shallow aquifer, which was effective in

RESULTS AND DISCUSSION

The groundwater chemistry profiles from the multi-level piezometers effectively delineated the vertical extent of leachate impacted groundwater in the aquifer downgradient from the landfill. In particular, field measurement of fluid electrical conductivity [EC] was a diagnostic measurement for identification of leachate impact. A strong correlation between fluid and bulk EC values was evident, both for surface and borehole electrical techniques, underscoring the effectiveness of these techniques as rapid screening tools for leachate impact in groundwater. The surface transects in particular provided valuable insight into the distribution and intensity of leachate impact within the aquifer that is not available from other techniques. The gamma logs identified thin, fine-grained layers in the sand profile that resulted in steep chemical and vertical hydraulic gradients within the aquifer.

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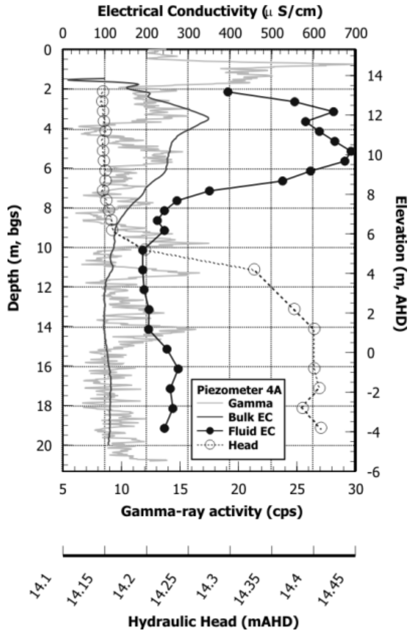

Fig. 1. **Comparison of bulk and fluid EC, gamma log and vertical hydraulic head values in a multi-level piezometer, with leachate impact evident in the upper aquifer.**

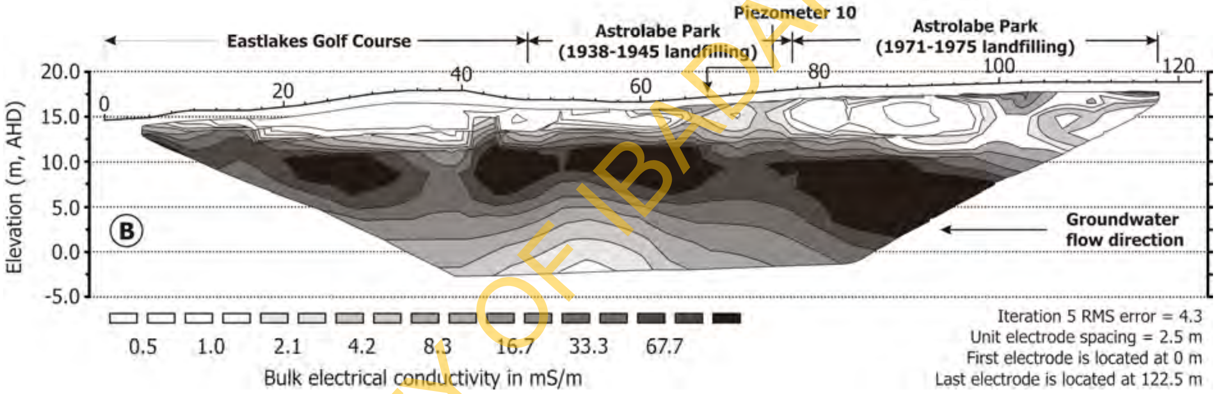

Fig. 2. **Electrical image from a surface resistivity transect parallel to groundwater flow beneath and downgradient from the landfill.**

CONCLUSIONS

The use of complementary high-resolution investigation tools provided a robust characterisation of leachate impact in shallow groundwater downgradient from a landfill, and has validated the efficacy of surface and borehole electrical techniques for characterising landfill leachate impact to groundwater in a shallow sandy aquifer. The methods can provide rapid and economical assessments in the right environmental settings that correlate strongly with measured groundwater quality, and can be used to optimise additional investigation efforts.

REFERENCES

Acworth, R.I. and Jorstad, L.B. (2006), Integration of multi-channel piezometry and electrical tomography to better define chemical heterogeneity in a landfill leachate plume within a sand aquifer. Journal of Contaminant Hydrology, 83 (2006), 200-220.

Jorstad, L.B., Jankowski, J. and Acworth, R.I. (2004), Analysis of the distribution of inorganic constituents in a landfill leachate-contaminated aquifer. Environmental Geology, 46 (2004), 263-272.

Jorstad, L.B. (2006), Analysis of variation in inorganic contaminant concentration and distribution in a landfill leachate plume: Astrolabe Park, Sydney, Australia. Ph.D. dissertation, University of New South Wales.

STRATEGIES IN MANAGING RISK OF LANDFILL GAS MIGRATION

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INTRODUCTION

Landfill Gas (LFG) has been utilised for electrical power production for over 30 years. Historically the utilisation of LFG has been the undertaken by organisations where the primary objective is the commercial sale of the electrical power to the state utility company and/or to increase profitability of the project via feed-in tariffs or carbon trading schemes. However, in harvesting the 'low hanging fruit' there is a portion of the LFG that is not collected.

In common with other extractive industries there is a law of diminishing returns i.e. as the resource depletes it becomes increasing expensive to extract it. Eventually, due to the inevitable drop in LFG flow and methane concentration there is a point where extraction of the LFG ceases. This can come about by a number of reasons but most commonly as a result of an operational decision by the management of the site or technical difficulties associated with combusting low flow and concentration methane.

On landfills that are geographically remote or where there is not sufficient LFG generation rates to offset the cost of installing a Gas Collection System (GCS) the LFG can be left to freely migrate laterally or vent to the atmosphere. It is usually when an elevated risk is identified by an interested party that a chain of events is initiated that sometimes results in the requirement to control the LFG. However, the methods used for LFG extraction can be implemented more efficiently by a combination of varying factors including the type of plant and infrastructure, and how it is managed.

BACKGROUND AND AIMS

The Garden Island landfill located in Port Adelaide, South Australia (the site) is located in a sensitive coastal environment, is unlined and prior to 2005, was uncapped. LFG is being generated and is expected to continue beyond 2030, but no GCS had been installed on the site. Methane has been recorded above 1,000 parts per million (ppm) venting through the surface at various locations around the site. Methane concentrations above 1.25 % by volume/volume (v/v) have also been reported in perimeter monitoring boreholes located outside the waste mass.

The overall aim of the project was to appropriately manage the LFG and mitigate the human health and environmental risks it posed to maintain a safe, positive land use balance over the long-term. Compliance targets of 500 ppm for surface fugitive release and methane concentrations of 1.25 %v/v for perimeter boreholes were set to measure performance of the GCS.

An innovative methodology for managing LFG was implemented with a site specific approach to design, construction and operation of an effective system to control LFG emissions in the areas of concern to the required performance requirements. The purpose of this presentation is to summarise the design and installation of these features and how they have resulted in an improvement of the management of LFG, and therefore reduced risk, on and off the site.

RESULTS

Following approval of a design concept a GCS was installed that comprised of the main innovative features. These were installation of an 'Ecoblanket' surrounding specific areas on the perimeter of the landfill, installation and operation of Impact Wells, and installation and operation of a low calorific flare.

A relatively long proportion of the perimeter of one of the landfill cells was in an uncapped state where the waste mass met the underlying marine sediment. Construction and demolition (C&D) waste was present over this area, presenting a porous structure for LFG migration off-site. The area was reinstated using imported clay, but in addition an ‘Ecoblanket’ was installed using composted mulch impregnated with native grass seeds. The Ecoblanket had a combined effect of providing a medium for microbial, which can aid in microbial oxidation of methane, and plant growth to mitigate wind and water erosion.

The design involved the installation 6 m deep Impact Wells by adapted earth moving plant. The system was modified and developed following extensive deployment of the technique in other parts of the world. The wells were spaced five metres apart over 100 linear metres in the areas where surface and off-site emissions were recorded. The impact wells in combination with deeper drilled extraction wells, created an effective vacuum ‘curtain’ around the site perimeter.

Conventional flares that combusted methane concentration from 25 to 40 % v/v were used for over 3,000 hours at the start of the project to test whether the compliance targets could be met. This was achieved when measured on the surface of the landfill and at the perimeter boreholes. Figure 1 shows the rapid drop in methane concentration following implementation of the system (dashed black line). The objective was long-term management of the landfill and as methane concentrations were reducing, a low calorific landfill flare (Low-cal) was deployed so that the system could run autonomously without the risk of repeated shutdown.

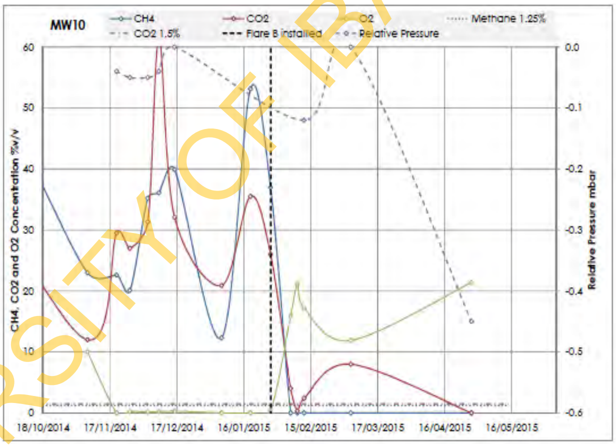

Fig. 1. LFG concentrations over time at perimeter monitoring well MW10.

CONCLUSIONS

A combination of novel GCS, operating protocols and flaring equipment were successfully designed, installed and managed at the site. This resulted not only in a reduction of fugitive release of LFG through the site surface but also to reduce lateral migration of LFG. One of the main innovations was that a flare was deployed that could sustainably combust methane at over 1,000 ^{0}C whilst ranging in concentration from 12 % up to 35 % by volume. The Low-cal flare’s wide operational range meant it could extract the hard to reach LFG at the perimeter of the site and its flexibility meant very little intervention was required by the operators and reducing long-term risk at the site.

ACKNOWLEDGEMENTS

This project was supported by the Western Region Waste Management Authority, Renewal SA, SA EPA and Tonkin Consulting.

AN AUSTRALIA-WIDE ASSESSMENT OF PERSISTENT, BIOACCUMULATIVE AND TOXIC CHEMICALS (PBTS) IN LANDFILL LEACHATES

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INTRODUCTION

A large number of chemicals with persistent, bioaccumulative and toxic properties (PBTs) have been used in industrial (e.g. pesticides) and household consumer products (e.g. flame retardants in plastics) over previous decades (Alaee et al., 2003, Fiedler et al., 2010). Due to concerns regarding human and environmental health, the manufacture and use of many PBTs has been phased out worldwide, and a new generation of replacement chemicals are now in use. Once products reach the end of their useful lives they are typically disposed of in landfills, and any associated chemicals may desorb into leachate. Despite their phase out, waste may still be entering landfills that contain many PBT chemicals, creating a potential contemporary and future risk of their release into surrounding environments (Weber et al., 2011). For many PBT chemicals, there are no regulatory requirements for their testing and so the types and levels in Australian landfills are largely unknown.

In 2014, leachate was collected from 27 landfills across Australia. Participating landfills covered a range of waste types accepted, ages, sizes, operational statuses and climate conditions to determine the levels and types of PBTs in landfills and whether there were relationships between PBT concentrations and landfill characteristics. The leachate was chemically extracted and analysed for 73 PBTs that included several classes of flame retardants, industrial chemicals, pesticides and herbicides.

METHODS

Leachate grab samples (2 L) were collected by landfill employees and shipped to Entox to undergo two extraction methods. An aliquot (250mL) of leachate was extracted by sonication (30 mins) with 100mL of dichloromethane (DCM) followed by liquid-liquid manual shaking (2 x 50mL; DCM). Extracts were combined, concentrated and subjected to clean-up using silica/ aluminium oxide cartridges, followed by a second concentration step under N_2 and passed through a florisil cartridge for further clean-up. The final extract was split for analysis and analysed using either gas chromatography mass spectrometry (GCMS) for industrial chemicals, brominated flame retardants and pesticides; and liquid chromatography mass spectrometry (LCMS) for brominated flame retardants. A second aliquot of leachate (50mL) was loaded onto sorbent cartridges at a rate of 10 mL/ min. Cartridges were dried and eluted with acetone, methanol and DCM, before concentration and final clean-up using Envicarb cartridges. Extracts were concentrated under N_2 to 1mL and samples were analysed by LCMS (for perfluorinated chemicals, herbicides and organophosphate flame retardants).

RESULTS AND DISCUSSION

Of the 73 PBTs that were analysed, 59 were detected in leachate including 14 that were detected at >50% of landfill sites. Frequently detected PBTs included the brominated flame retardant BDE-99 (52% of landfills; maximum 1100 ng/L) and the pesticide dieldrin (48% of landfills; maximum 110 ng/L) that have been phased out and listed as Persistent Organic Pollutants (POPs) under the Stockholm Convention. The perfluorinated chemicals perflurooctanoic acid (PFOA) (maximum 7.5 µg/L) and the listed POP perfluorooctanesulfanoic acid (PFOS) (maximum 2.7 µg/L) were the most frequently detected in 100% of landfills. Six of the nine organophosphate flame retardants analysed were detected in more than half of landfills. Due to the unique differences of landfill characteristics (such as age or waste type) between sites, correlation of landfill types to PBT profiles was difficult. However, overall there appeared to be an association of increased concentrations of brominated flame retardants and pesticides with municipal (household) solid waste landfills (Figure 1). Conversely, landfills that did not accept municipal waste and only accepted waste such as contaminated soil, building and construction rubble, and shredder floc had on average, higher concentrations of the perfluorinated chemicals (bottom, Figure 1).

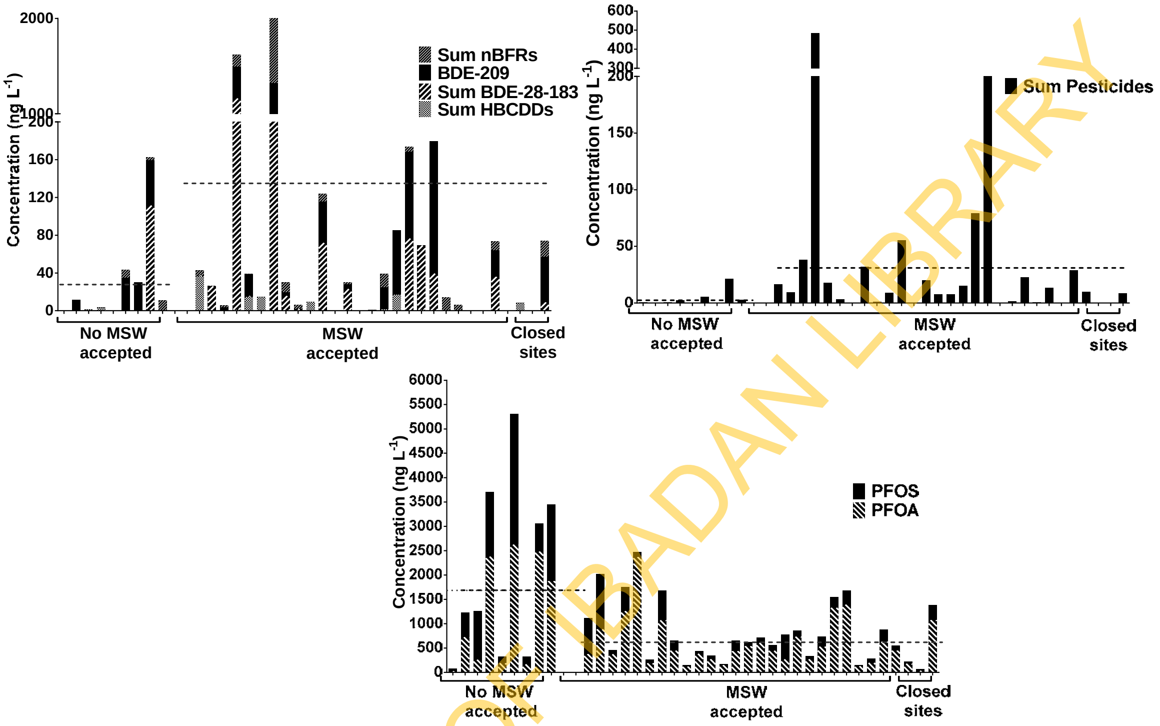

Fig. 1. Total concentrations (ng/L) of a range of brominated flame retardants (top left), organochlorine pesticides (top right) and perfluorinated chemicals (bottom) in operating landfills that accept and do not accept household waste. Dotted lines represent the average sum concentrations.

CONCLUSIONS

The results of this study may help to establish a national baseline for PBTs in leachate that could be useful in measuring the impact of any regulatory action on chemicals. It could also be informative in the development of a nationally consistent approach to testing, analysing and reporting of PBT chemicals in leachate in Australia. The results indicate that landfills can continue to be a source of PBTs for decades after regulatory action, and highlight the challenges associated with the disposal of such long-lived chemicals.

REFERENCES

ALAEE, M., ARIAS, P., SJÖDIN, A. & BERGMAN, Å. 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment international,* 29**,** 683-689.

FIEDLER, S., PFISTER, G. & SCHRAMM, K.-W. 2010. Poly-and perfluorinated compounds in household consumer products. *Toxicological and Environ Chemistry,* 92**,** 1801-1811.

WEBER, R., WATSON, A., FORTER, M. & OLIAEI, F. 2011. Review Article: Persistent organic pollutants and landfills-a review of past experiences and future challenges. *Waste Management & Research,* 29**,** 107-121.

EFFECTIVE RESIDENTIAL REDEVELOPMENT OF A METHANE-PRODUCING FORMER LANDFILL SITE, MELBOURNE, VICTORIA

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INTRODUCTION

A residential development for 208 townhouse dwellings has been undertaken across a former landfill site in south-east Melbourne, Australia. The purpose of the assessment was to provide the State environmental regulator with information on the contamination status of the site and the consequent implications for the suitability of the site for residential use. More specifically, the site investigations by the authors aimed to determine the presence of and the potential risks posed by any ground gas (esp. landfill gas, LFG) both on-site and off-site. The potential for LFG migrating from the site to off-site locations, from deep within the backfilled material to shallow surface locations and then into the atmosphere were assessed.

CONDITION OF THE SITE

The site was a former sand quarry where 50 years of sand extraction occurred to depths of approximately 20 metres. Following completion of sand extraction, the site was reclaimed between 1976 and 1989 by progressive, *ad hoc* backfilling of approximately 304,000 m^3. An engineered cover layer was not installed. Within deeper fill on the site, the non-natural material observed was:

a) timber/woody material was observed in zones of variable thickness in the northern area of the site and east to west across the site; and
b) building material, which also contained timber, was identified in zones of variable thickness in the western and northern portion of the site.

The quantity of the organic material within the reclaimed area is unknown, but based on the visual assessment during geotechnical drilling completed by others, and the site investigations described herein, the authors estimate approximately 2-3% organic material (by mass) occurs in the fill.
Local lithology comprises Tertiary marine and non-marine sands, clays, ferruginous sandstones and gravels. Groundwater intersection depths within the filled material at the site and Brighton Group aquifer typically mirrored the topography, with the initial water strikes along the western boundary being in the order of 14.0 metres below ground level (mbgl), decreasing to 8.0 mbgl along the eastern boundary. The groundwater was found to lie within the fill material was in hydraulic continuity with the adjacent aquifer.

OCCURRENCE OF LANDFILL GAS

For the investigation conducted by the authors, 27 LFG monitoring wells were installed in 2010 to a maximum depth of 14 mbgl around the perimeter of the site within the Tertiary Brighton Group Formation. Also installed at that time were four wells installed to 4.0 mbgl inside the landfilled area. The LFG monitoring wells were advanced using a combination of push tube, solid stem auger and diamond coring. The LFG wells were installed using either a nested well design (discrete depths) or were fully cased depending on the identified geology. Sampling of these 27 LFG monitoring wells was undertaken on nine occasions between September 2010 and January 2011 using a landfill gas meter. Continuous measurements of LFG were undertaken at three locations during December 2010 and January 2011 using a proprietary “GasClam” down-hole data logger (Morris et al, 2008; CL:AIRE, 2011).

A summary of the results is provided below:

a) methane was reported at all six central wells with concentrations ranging from 0.0%v/v to 69.9%v/v. Concentrations of methane in excess of 1%v/v were observed in five of the central wells;
b) carbon dioxide concentrations ranged from 0.0%v/v to 32.7 %v/v with concentrations reported in excess of 1.5%v/v at all six locations;
c) Positive gas flow rates were measured at values between 0 and 24.4 litres/hour (l/hr).

In addition to sub-surface monitoring, surface emissions of LFG were also monitored using a 0.16m^2 flux hood (CIRIA, 2007) at 33 randomly selected locations over the site in October 2010. A walkover to determine the presence of hot spot locations using a hand-held flame ionisation detector (FID) was also completed at that time. Additional flux hood monitoring was conducted at seven locations in May 2011, which was focused at locations where hotspots were identified. This work reported one concentration above the limit of reporting; the concentration of methane was reported to be 42 mg/m^3 which corresponds to a flux hood emission rate of 0.53 mg/m^2/min.

DEVELOPMENT APPROACH INCORPORATING LANDFILL GAS ASSESSMENT

Based on UK-based semi-quantitative methods for assessment of risk (CIRIA, 2007; BS8485, 2007, NHBC, 2007), the site was classified as Characteristic Situation Value (GSV) of 3 for any development (including slab on-grade residential). This GSV was defined as a “moderate risk” (using CIRIA terminology), and is representative of inert waste, old landfills. House design comprised a piled slab foundation, with a proprietary gas resistant membrane and underlying passive venting using granular blanket and embedded vent pipes. The first stage of 90 contiguous townhouses (ie blocks of terrace houses ranging from 54m^2 to 675m^2 in vented floor area) was completed and occupied during 2013. LFG concentrations were monitored during construction, and continued to be monitoring during occupancy, in 10 on-site soil gas bores and 17 on-site nested bores. Monthly monitoring of vent riser pipes from the houses constructed to date shows a maximum of 8.5% v/v CH_4 and 6.7% v/v CO_2, and a maximum flow rate of 1.8 l/hr (estimated methane GSV of 0.2). This data shows good consistency with the LFG design parameters.

CONCLUSIONS

The paper concludes that construction work has not impacted lateral migration of LFG from the site. Gas protection systems in houses are performing as intended. Post-construction monitoring to date has shown good levels of agreement with design assumptions for landfill gas concentration and flow rate, confirming a moderate risk classification of the site.

REFERENCES

British Standard (2007) *Code of Practice for the Characterization and Remediation from Ground Gas in Affected Developments*. BS8485:2007.

CIRIA Report C665 (2007) *Assessing risks of hazardous ground gases to buildings*. Prepared by S. Wilson, S. Oliver, H. Mallett, H. Hutchings, G. Card.

CL:AIRE 2011 The *Utility of Continuous Monitoring in Detection and Prediction of "Worst Case" Ground-Gas Concentration, Contaminated Land: Applications in Real Environments*, Research Bulletin RB13, February.

National House-Building Council (NHBC) (2007) *Guidance on Evaluation of Development Proposals on Sites Where Methane and Carbon Dioxide are Present*. Report Edition No: 04.

Morris, P, Todman, M, Boult, S. (2008) Improved Ground-Gas Risk Prediction Using in-Borehole Gas Monitoring, Consoil 2008: Theme C - Site Investigation: Monitoring and Screening. p36-44.

LNAPL EXTRACTION PRACTICABILITY ASSESSMENT — FORMER HAZARDOUS WASTE LANDFILL, TULLAMARINE, VIC, AUSTRALIA

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INTRODUCTION

LNAPL at Tullamarine Landfill was identified within landfill cells during an upgrade to the leachate extraction system in the mid 2000's. The LNAPL comprised a mixture of constituents, including PCBs at concentrations in excess of the landfill licence conditions. In 2009, the Environmental Protection Authority (EPA) issued a Pollution Abatement Notice (PAN) for the aftercare management of the Site which, amongst other directives, included the requirement to implement a Liquid Waste Management Plan (LWMP).

In order to satisfy the objective of the LWMP, an LNAPL extraction trial was undertaken and an LNAPL Extraction Practicability Assessment developed. This presentation provides an overview of the process, including the outcomes of the extraction trials, the findings of the Practicability Assessment and the involvement of the active community group.

METHODS

Following estimates of LNAPL mass and a remediation technology appraisal assessment, an LNAPL trial program was developed and implemented to assess the feasibility of LNAPL extraction. The trial enabled the calculation of LNAPL Transmissivity, which together with other qualitative observations (ability to sustain pumping rates and ability to draw LNAPL from the waste material within the landfill cells) provided the metrics utilised to assess the viability of further extraction at the site.

The trial program findings provided the basis for the LNAPL Extraction Practicability Assessment and in particular the baseline for comparison against estimated natural mass losses.

Theoretical natural mass loss estimates were derived for dissolution and biodegradation mass losses based on LNAPL chemistry, whilst quantitative estimates of volatilisation mass losses were derived using data from the sites landfill gas extraction and treatment system.

In the context of the natural versus engineered mass loss estimates, a net benefit analysis, using sustainability principles, was undertaken as a means of addressing community concerns and contextualising the relative benefits of active remediation in the context of the site's risk profile.

As part of the community consultation process, community meetings were held during the course of the trials and the practicability assessment to ensure that community concerns were addressed during the process.

RESULTS AND DISCUSSION

LNAPL extraction trials conducted in 2014 demonstrated that Site conditions would not support long-term extraction and that the LNAPL is functionally immobile.

Based on the trial results, it was considered that LNAPL clean up has been completed to the extent practicable and that the regulatory remediation drivers have essentially been met from a technical perspective, noting that the risks from the LNAPL were considered to be low. However, it was considered that community concerns associated with societal factors and preservation of intergenerational equity still provided potential remediation drivers.

Conservative estimates indicate hydraulic recovery would require between 350 and 1,400 years of implementation to extract the estimated recoverable portion of the LNAPL (4 to 7 ML), noting that in reality, the required timeframes would be significantly longer and substantial volumes of LNAPL (recoverable and residual) would remain trapped in the waste due to constraints identified during the extraction trials. In addition, an assessment of natural mass depletion processes was conducted, which indicated that significant LNAPL mass loss, relative to continued hydraulic recovery scenarios, would occur via volatilisation, biodegradation and dissolution.

With consideration of the limited risk and substantial natural mass losses, a net benefit analysis was conducted to evaluate potential impacts to the environment and community that could result from implementation of additional active remediation activities.

CONCLUSIONS

The LNAPL Extraction Practicability Assessment indicates that the Tullamarine Landfill LNAPL clean up has been completed to the extent practicable (noting that up to potentially 18 ML of LNAPL remains within the landfill cells), natural mass losses will continue to occur at appreciable rates and there is no net benefit in terms of implementing further remedial efforts. In the absence of active remediation measures (aside from continued operation of the landfill gas recovery system and maintenance of the landfill cap), the Sites Post Closure Management Plan will serve as the key mechanisms for the assessment of ongoing risks and potential implementation of contingency measures to manage potential risks to health and the environment in the future.

REFERENCES

API, 2012. *LNAPL Transmissivity Workbook: A Tool for Baildown Tests Analysis and User Guide*. American Petroleum Institute. (API, 2012).

ITRC. (2009). *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org. December 2009.

ITRC. (2009b). *Evaluating Natural Source Zone Depletion at Sites with LNAPL*. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org. June 2009.

Johnston.C.D., (2010). *CRC Care Technical Report 18 – Selecting and Assessing Strategies for Remediating LNAPL in Soils and Aquifers*, CSIRO Land and Water, September 2010.

THREE REASONS TO CONSIDER SUSTAINABLE REMEDIATION A GLOBAL PERSPECTIVE AND A MUTUAL INTEREST

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INTRODUCTION

Over the last decade we have seen many developments in the field of Sustainable Remediation. In many countries Sustainable Remediation Forums were founded, and NICOLE — the Network on Industrially Contaminated Land in Europe — started its own working group, and Common Forum — a network of Policy makers from the European member state — started the debate on risk informed remediation in 2002. NICOLE published its Road Map for SR in 2010, and in 2013 The Common Forum and NICOLE jointly published a Joint Position Statement on Risk Informed and Sustainable Remediation, a statement that clearly expresses the common objectives of the Industry and the Policy makers to move to a sustainable approach for Remediation. Currently the JPS is translated into 10(!) different European languages, which underlines its importance. We will give an overview of international initiatives and the obvious reasons – with example cases - to start them.

A COMMON UNDERSTANDING, THREE REASONS

Usually the definition of SURF-UK for Sustainable remediation is used:

> ‘the practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact and that the optimum remediation solution is selected through the use of a balanced decision-making process’

Behind the definition also lie 6 principles. SR should be transparent, embody no unacceptable risks, and based upon sound science. If applied correctly this does imply a change of approach. No longer a concentration targeted objective is key, but a focus on the benefits and impacts of social, economic and environmental indicators. These two approaches may be alike or overlapping, but often there is a significant difference. Some examples and reasons:

Social: The risk for Human beings is the most relevant element. Above all these should be absolutely minimized as much as possible. In many cases the actual risk for Humans as a result of contaminants in soil and groundwater is limited or absent. During a Nicole workshop in 2008 it was demonstrated that the execution of a specific remediation embodied higher risks (accidental risks) than the contaminants. There are 3 documented cases in the Netherlands with deadly accidents as a direct result from the remediation. One example will be highlighted.

Environment: The environment is not only about soil and groundwater quality. The production of waste and carbon dioxide and the use of non-renewable sources should also be considered. It is obvious that soil protection is very important to avoid newly contaminated soil, but historical contamination is another issue. Given the fact that a site is contaminated, what is the optimal way forward, driving 10.000 lorries through a neighbourhood, producing exhaust fumes, consuming diesel and causing accidental risks? An example.

Financial: Remediation entails cost. The expenses should be carefully balanced with the benefit every dollar spend does deliver in terms of risk reduction or improvement for the environment. A careful balance of benefits and burdens. An example of a railroad yard remediation.

NICOLES ROAD MAP, INCLUDING MORE REASONS

The ROAD MAP that was produced by the working group sustainable remediation comprises a decision process. A process that aims at a careful balancing of sustainability indicators, and moreover at a full agreement of all stakeholders. That the option selected is regarded by all as the most sustainable way forward is in itself an important element of the social aspect of SR. The Road Map will be briefly explained. Currently 8 example cases of the application are available at www.nicole.org . An overview table of these cases with evaluation format will also be presented showing the added value of considering sustainability. Available are cases in Italy, Madeira, UK and the Netherlands, and more to come.

THE IMPORTANCE OF THE JOINT POSITION STATEMENT

In 2013 Common Forum and NICOLE agreed on a Joint Position Statement (some parts will be explained in the presentation). By all members this is regarded of big importance, since the major barriers towards the implementation of SR lies with the local authorities and regulators. Convincing them with clear cases and the support of Common Forum is a first step in moving towards wider acceptance. Having the JPS translated into the different languages by both industry members and the national policy makers further assures that the JPS fits the national policy framework. The large amount of translations proves that there is broad support throughout Europe.

THE INTERNATIONAL SURF COMMUNITY

More globally 10–12 SURFs communicate across the globe about the developments and their progress. NICOLE is linked to this network and in close cooperation. They share white papers, frameworks and guidelines. There is cooperation for The Sustainable Remediation conference (SUSTREM), that is organised every 2–3 years.

SUSTAINABLE PRACTICE APPLICATION TO AUSTRALIAN AND REGIONAL REMEDIATION PROJECTS

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INTRODUCTION

Following a decade of international sustainable remediation (SR) practice development, the implications and benefits of the approach are now evident in Australian and international tools and case studies. SR concepts, which apply from regional planning to remediation technology selection scales, appear in guidelines and frameworks for remediation, reflected in drafting of the International Standards Organisation ISO on Sustainable remediation 2015. The concept is consistent with Ecologically Sustainable Development policies and guidelines in state legislations, operating at the next level of detail, and is currently being considered in Australian National Remediation Framework development. Site owners are recognising the value to remediation approvals, operational design, and stakeholder engagement, of using an SR approach to contaminated site remediation project design and implementation.

METHODS

The material presented is based upon examination of the following aspects of SR development and practice in Australia and overseas:

a) A review of published international and Australian SR practice tools;
b) Development of project design and technologies selection tools;
c) Identification of SR concepts in international and Australian frameworks;
d) Examination of the draft ISO on Sustainable remediation 2015[1];
e) Identification of the benefits to approvals, design, and stakeholder engagement;
f) Analysis of illustrative Australian and international case studies.

RESULTS AND DISCUSSION

SR practice tools

A definition of SR used in Australia and New Zealand is “a remediation solution selected through the use of a balanced decision making process that demonstrates, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than any adverse effects” (SuRF ANZ 2015). A number of international SuRF organisations have published frameworks, and tiered project development and technology selection guidance, which has been applied to significant remediation projects internationally (SuRF ANZ 2015). Several international consultancies have developed sustainable remediation assessment tools (SustRem 2014).

Design and Remediation Technology Selection

SuRF ANZ recently published a soil remediation decision-making tool based on typical case study cost, environmental and social parameters (SuRF ANZ 2015). An analysis of relative sustainability rating and direct cost prediction for 15 potential cleanup technologies indicated that most of the more sustainable technologies on balance exhibited comparable or lower direct project costs i.e. are on the right hand side of the graph in Figure 1.

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[1] The Sustainable Remediation Forum of Australia and New Zealand (SuRF ANZ) worked on draft ISO development.

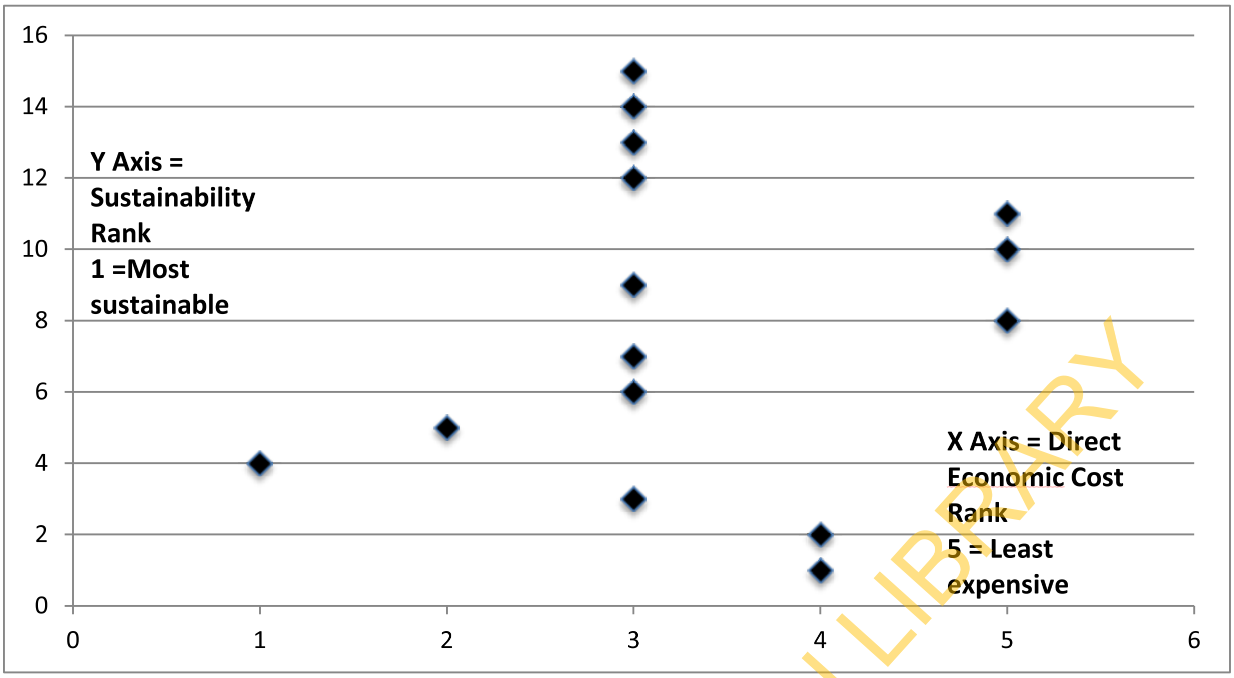

Fig. 1. Estimation of Sustainability rank V Technology direct cost rank for Fifteen Soil Remediation Technology Options.

Approvals, operational design, and stakeholder engagement in remediation projects in Australian and international case studies

The case study on the Lednez site, located on the Rhodes Peninsula in Sydney, reflects important early SR development in the Australian planning, regulatory, and community engagement contexts. Lessons learned, and more recent remediation tool selection guidance in Australia are now available to support more uniform and widespread sustainable remediation regulatory dialogue, project design, and project implementation in Australia and the region (SuRF ANZ 2015).

It is anticipated that the draft International Standards Organisation ISO on Sustainable remediation 2015 will consolidate best practice and be useful for both developed and developing global remediation guidance.

CONCLUSIONS

The benefits which SR practice in Australia and the region offer include:

a) A more transparent and evidence based process for remediation decision making;
b) Balancing of environmental, economic and social aspects of the project early in remediation project design;
c) Consideration of integrated local land use planning and statutory and cultural opportunities e.g. brownfields urban renewal;
d) Reduced project delivery costs through technology optimisation and regulatory/stakeholder communication.

REFERENCES

SuRF ANZ (2015) A Framework for Assessing the Sustainability of Soil and Groundwater Remediation (and associated links), Sustainable Remediation Forum of Australia and New Zealand, www.surfanz.com.au (accessed 15 April 2015).

SustRem (2014) Proceedings of the 3rd International Sustainable Remediation Conference, Ferrara, Italy http://www.sustrem2014.com/final_conference_documentation.html (accessed 15 April 2015).

REDUCING CONTAMINATED MATERIAL DISPOSAL VOLUMES – A SUSTAINABLE AND COST EFFECTIVE REMEDIATION APPROACH

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INTRODUCTION

This case study demonstrates sustainable delineation and segregation techniques applied to over 10,000 m^3 of historic fill material at a site adjacent to a long standing rail yard. This approach resulted in a significant reduction in contaminated material requiring off-site disposal. Contaminants of concern included asbestos containing material (ACM), hydrocarbons and potential acid sulfate soils (PASS) and consequently reducing cost. The project applied the following approach: (i) grid based delineation of hydrocarbon contamination 'hotspots' allowing targeted remediation, (ii) a five stage physical screening process to remove ACM and other rubble and (iii) segregation approach designed to produce material that could be used in the construction phase. The segregation approach reduced imported fill volumes and allowed direct reuse of segregated material in the construction phase. The savings to the project were estimated to be several hundred thousand dollars. The project was subject to a third party Contaminated Site Auditor review.

The project demonstrated an effective approach to integrating the experience of construction engineers, environmental consultants, geotechnical engineers and the client requirements to develop a pre-construction methodology; and therefore, allowing a smoother and cost effective construction phase.

Project background

The City Busport Alliance (CBA), an alliance between Public Transport Authority and Brookfield Multiplex, engaged GHD Pty Ltd (GHD) to develop a Spoil Management Plan for the site of the New Underground Bus Station (NUBS) in Perth, Western Australia (the Site).
The Site is located within a former wetland area historically reclaimed with uncontrolled fill materials and developed for the Perth Central Train Station, Bus Station and associated rail yard.

The geology of the Site underlying the fill layer was defined by a peaty lake sediment layer, Spearwood Sands and various units of the Guildford Formation. The natural geological units were PASS. The groundwater table of the superficial aquifer was approximately in line with the peat layer.

The construction for the NUBS was a 'top down' construction in which the pilling, diaphragm walls and roof slab were constructed first. Then the spoil material was excavated from under the roof slab, which limited any opportunity for effective segregation of fill, peat and natural PASS materials during construction. This meant the entire spoil volume would require disposal to landfill, treated as ASS, and potentially containing asbestos.

OBJECTIVES

The objectives of the remediation works were to: (i) minimize the amount of imported fill material required for construction, (ii) maximise the direct re-use of segregated materials in the construction phase works and (iii) apply the principals of sustainable remediation to the remediation design.

SCOPE OF WORKS AND RESULTS

In line with the objectives, GHD developed a cost effective waste segregation strategy to provide the most sustainable outcome, which included the following:

(a) Removal and validation of hydrocarbon contamination 'hotspots' in the shallow fill.

(b) Excavation of the remainder of the uncontrolled fill and on-site screening. An automated soil screener was used to separate excavated soil into five fractions; and thereby; removing entrained anthropogenic constituents including inert rubble, rail ballast, steel, metal pipes, plastics, and minor asbestos fragments (≥50 mm) for off-site disposal as Special Waste Type 1 at an appropriately licensed facility.

(c) Inspection and validation testing of screened fill (<50 mm) confirmed no visible ACM and no asbestos fibre/fines detects above 0.001% w/w. Asbestos, observed to be in good condition within the oversize fraction was below the Department of Health (DoH 2009) guideline value for residential (i.e. 0.01% w/w). The screening process was found to be effective in removing asbestos fragments and the screened fill was characterised as free of asbestos, non-ASS with concentrations below the relevant Department of Environmental Regulation ecological investigation levels (DER 2010 and DER 2009) and was suitable for re-use on-site.

(d) Air quality monitoring for asbestos fibres was completed in the vicinity of the screening operations during the screening process. All air quality monitoring results were below the method detection limit of 0.01 fibres/mL.

(e) Selective excavation and removal of the peat layer (PASS and geotechnically unsuitable for re-use) was completed and the peat material was transported off-site for treatment and disposal or re-use as soil conditioner.

(f) The validated screened fill sands were backfilled over the Spearwood Sands (PASS) and levelled to form the casting bed of the NUBS roof slab.

(g) After completion of the roof slab the screened fill was excavated with the deeper natural soils (Spearwood Sands and Guildford Formation) as part of the 'top down' construction of the NUBS was deemed suitable for re-use at another site (only minor ASS treatment was required).

CONCLUSIONS

The net result of our innovative segregation strategy was that only less than 10% of the 76,000 m^3 excavation was disposed of to landfill, hugely reducing the cost and extending the life cycle of the material. Due to this sustainable approach of pre-construction segregation and screening activities, all sandy spoil generated from the 'top down' excavation was suitable for reuse after minor ASS treatment.

REFERENCES

Department of Health (2009) *Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia,* Department of Health, Toxicology Branch, Perth, Australia.

Department of Environment Regulation (2009) *Landfill Waste Classification and Waste Definitions 1996 (As amended December 2009),* Department of Environment and Conservation, Waste Management Branch, Perth, Australia.

Department of Environment Regulation (2010) *Assessment Levels for Soil, Sediment and Water*, Contaminated Sites Management Series, Department of Environment and Conservation, Land and Water Quality Branch, Perth, Australia.

REMEDIATION IN THE CONTEXT OF GLOBAL SUSTAINABILITY

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INTRODUCTION

The global remediation industry is immense with annual expenditures for on-shore soil and groundwater remediation in the multi-billions. Whilst much regulation allows a risk-based approach and recognises complete clean-up is often not possible, there remains a great deal of remediation undertaken in response to community and/or regulatory drivers even when risks are absent. Further, the human health levels often driving remediation are extremely conservative when placed in context with the risk associated with activities humans carry out frequently and often daily. When these activities are required on a remediation project (for example driving to site) a reasonable assessment may determine the risk to human health of remediation to be larger than the risk from the contaminants in the ground. Such assessments are often seen as “pushing for do nothing or spend less” and yet to be given due consideration.

With climate change and water supply becoming species threatening issues, it is proposed the completion and review of stricter assessments are imperative to ensure remediation is providing a net benefit and adding to the overall sustainability of the planet. This paper looks at the overall net benefit of global remediation and places this in context with broader issues such as climate change, world poverty, and energy, water and food supply.

A secondary theme is the relative merits of sustainability metrics. For example, is 1,000 tonnes of carbon dioxide worse than 100 tonnes and if it is, what is the significance of the impact? If preservation of human life is a key aspiration, should remediation approaches where distance travelled is high (e.g. remote sites) be weighted much lower due to the high risk of accident or injury?

This work is founded on net benefit assessments undertaken by the author for operating remediation systems in Australia where the objective was to highlight that continued operation was resulting in nil and often negative net benefit to humans and the environment. From this work and appreciating the big-picture issues facing humanity, it is apparent the net benefit of all activities including remediation must be assessed. The objective of this paper is to demonstrate the sense of this statement.

METHODS

Desk-top scale with data referenced from past net benefit assessments undertaken by the author and credible and cited sources for non-project specific data. The *Battelle et al* sustainable remediation tool SiteWise™ is used to calculate quantities such as carbon dioxide emissions from remediation systems.

RESULTS AND DISCUSSION

This paper compares and contrasts remediation quantities with big-picture quantities. For example, the potential impact on the water deficit and food supply of using electricity for remediation systems is presented using average values for water consumption per unit of electricity produced, water consumption per unit of grain produced and grain consumed per person per year. The potential contribution to climate change is presented in terms of the addition of carbon to the atmosphere from remediation.

CONCLUSIONS

The key conclusion of this paper is that remediation must be treated in a similar manner to other industries and endeavours with respect to sustainability. A truly sustainable approach must recognise the best approach may be no action or monitoring only and in these cases should find support from regulators and other stakeholders. This conclusion is supported by the findings of the work that illustrate even a small sub-set of remediation (in this case considered to be implemented for poor reasons) has notable secondary impacts.

REFERENCES

Aggidis et al. (2013). Global Food. Institution of Mechanical Engineers.

Various Contributors, National Research Council. (2013). Alternatives for Managing the Nation's Complex Contaminated Groundwater Site. National Academy of Sciences.

BP Oil. (2015). BP Energy Outlook 2035. bp.com/energy/outlook

Conner. R et al. United Nations Water. (2015). Water for A Sustainable World. UNESCO.

SiteWise^{TM}. Batelle and US Armed Forces. (2013). Sustainable Remediation Tool. Naval Facilities Engineering Command, Engineering and Expeditionary Warfare Centre.

THE NATIONAL REMEDIATION FRAMEWORK — TOWARDS HARMONISATION

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INTRODUCTION

The federal nature of Australian governance means that responsibilities are split between federal and state governments. Constitutionally, responsibility for land management and environmental protection lies with the states. Given the disparities in geology, soil types, climate and biota across the continent, differences have arisen in the management of these matters across the continent.

There is significant momentum to harmonise laws, regulations and guidance across states, with significant benefits for the national economy. The National Environment Protection Council has developed harmonised, legally mandated, national environmental standards, including national guidelines for the *assessment* of site contamination. Legal and political realities have meant that to date, complementary national guidelines for *remediation and management* of contaminated sites are not in place – in the meantime, all States have their own guidance for remediation and management which suits local needs, but which differs from one state to another, both in approach and in coverage of issues.

The proposed National Remediation Framework aims to harmonise the remediation and management of contaminated sites, and will promote cost effective and efficient site clean-up with optimal environmental, economic and social footprints for remediation and management, and will facilitate enhanced standards of professional practice across the country.

THE FRAMEWORK AND SUSTAINABILITY

A principal objective is to develop a national framework which facilitates optimisation of the environmental, economic and social footprints for remediation and management. Almost all environmental protection legislation in Australia incorporates sustainability principles, which are clearly applicable to site clean-up and management. To this end, risk based land management and sustainability concepts underpin the Framework.

FRAMEWORK DEVELOPMENT

The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) is funded by government and industry to carry out mission oriented research into the clean-up of contaminated sites. CRC CARE's remit also includes the harmonisation of regulatory guidance, which it is well placed to carry out, given its linkages with and access to state governments and industry.

A steering group comprising stakeholders from the petroleum and mining industries, the Defence Department, land development agencies, contaminated land consultants and auditors, and state and territory environmental protection agencies, has been established to provide strategic oversight for the development of the Framework.

STRUCTURE AND DEVELOPMENT

The steering group has agreed that the Framework should build on existing documentation and experience, and not impinge on the policy and legal decision-making prerogatives of the states and territories. The Framework comprises two parts:

Part 1: Philosophy - which includes principles for remediation (which are consistent with those for ecologically sustainable development), and

Part 2: Practice – which comprises practical guidance for practitioners for all steps of the remediation and management process - from the setting of remediation objectives and technology selection, to development and implementation of site remediation plans, to post-remediation auditing and the use of institutional controls for longer term management.

Part 1 has been completed, and it is expected that all draft guidance (ie Part 2) will be completed by early 2016.

Mechanisms for consultation with industry and governments are in place for draft guidelines as they are produced.

ENDORSEMENT

It is envisaged that governments will endorse the completed framework.

REFERENCES

CRC CARE 2013, *Identification of existing guidance for a National Remediation Framework*, CRC CARE Technical Report no. 28, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

CRC CARE 2013, *Defining the philosophy, context and principles of the National Framework for remediation and management of contaminated sites in Australia*, CRC CARE Technical Report no. 27, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Scott, K & McInerney, M 2012, *Developing a national guidance framework for Australian remediation and management of site contamination: Review of Australian and international frameworks for remediation*, CRC CARE Technical Report no. 22, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

OVERVIEW OF THE GUIDELINES FOR PERFORMING COST BENEFIT AND SUSTAINABILITY ANALYSIS OF REMEDIAL ALTERNATIVES

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INTRODUCTION

CH2M is currently developing a guideline for performing cost benefit and sustainability analysis of remedial alternatives, to be included within the NRF. Similar to all guidelines within the NRF, one of the aims of this guidance was to synthesise existing Australian and international guidance on the topic. However there are currently no Australian state or territory guidance documents related to cost benefit or sustainability analysis for remedial alternatives. In addition, the application of such economic principles as cost benefit analysis has not been regularly applied to site remediation in the Australian context. As such, an overarching guideline that both introduced the relevant concepts and provided a framework for conducting the analysis was required, as part of the NRF.

A particular focus of the guidance was for it to be user-friendly, scalable, and provide a robust, transparent and repeatable methodology.

SUMMARY

In order to formulate this guidance document CH2M drew on international literature, conventional economic literature regarding cost-benefit analysis and sustainability analysis, and prior knowledge of conducting such analysis in both remediation and conventional economic settings.

CH2M developed a table of contents, annotated outline, draft for discussion and final draft, with each document receiving feedback from CRC CARE and the NRF Steering Group prior to continuing on to the next phase.

A key development of this guideline has been the true integration of cost benefit analysis and sustainability analysis. This has been done by conducting a cost benefit analysis where applicable, and then using the outcome of that analysis as an input for the sustainability analysis (multi-criteria analysis). This is a novel approach, which has been adopted by another similar international guidance document since commencement of this project.

In addition to the guidance document, CH2M has developed a spreadsheet-based tool that automates much of the calculation. The purpose of this tool is two-fold; one is to remove the focus from the mechanical mathematics and place it on the decision making paradigm that comes from examination of the analysis output. The second is to provide a standardised way of presenting the data.

RESULTS AND DISCUSSION

The guideline is currently close to completion.

SUMMARY OF
FOUR NATIONAL REMEDIATION FRAMEWORK GUIDELINES

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INTRODUCTION

CH2M is currently developing four separate guidelines for inclusion within the National Remediation Framework (NRF).

These guidelines are:

- National Remediation Framework Guideline on Auditing
- National Remediation Framework Guideline on Remediation Validation and Closure
- National Remediation Framework Guideline on Institutional Controls; and
- National Remediation Framework Guideline on Long Term Monitoring.

SUMMARY

The *Auditing* guideline aims to harmonise existing guidance pertaining to the auditing of contaminated sites' remediation, for inclusion within the NRF. Whilst legislation and guidance varies across different Australian jurisdictions, the guideline aims to provide a clear and practical overview of the role of auditing of remediation in Australia and focus upon best practice. Key sections within the guideline include the purposes of auditing within the context of remediation, the role of the auditor and other stakeholders, the scope of a remediation audit and liabilities associated with the auditing process.

The *Remediation Validation and Closure* guideline aims to harmonise existing Australian and international guidance, as relevant to the validation of remedial works, for the purposes of achieving site closure. The guideline aims to provide an overview of validation approaches in the context of the most commonly applied remedial techniques in Australia and outlines the lines of evidence that may need to be collected to demonstrate the effectiveness of remediation. An overview of the steps required to achieve site closure is also provided, with details on contingency plans that may be employed where remedial targets are not achieved within a practicable time-frame.

Currently in Australia the approaches to the implementation of post remedial institutional controls varies greatly between jurisdictions. Therefore the *Institutional Controls* guideline aims to provide a harmonised approach to the best practice application of post remediation institutional controls while taking into consideration the variability in legal requirements within Australia. Key sections of the guideline include direction on when institutional controls are appropriate and how they can be effectively implemented.

The *Long Term Monitoring* guideline aims to harmonise existing Australian and international guidance relevant to post remedial monitoring. The guideline provides an overview of monitoring approaches in the context of the most commonly applied remedial techniques in Australia and outlines the lines of evidence, notably including the nature of the data that may need to be collected to demonstrate the effectiveness of remediation, and the requirement to continue monitoring. Key sections of the guideline include the process of developing a long term monitoring plan for a site and the components which should be considered (such as the nature of the data and the frequency of collection), as well as a summary of conceptual site models and their importance in undertaking long term monitoring at a site.

IDENTIFYING AND ASSESSING CONTAMINATED SITE REMEDIATION OPTIONS

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CRC CARE is developing a National Remediation Framework (NRF) for the remediation of contaminated sites in Australia. The NRF will comprise a series of documents to provide guidance on the practicalities and options for cleaning up contaminated sites.

This paper provides an introduction to work that has been carried out for the NRF program relating to the identification of remediation options, and the assessment of particular remediation technologies.

The work has involved the preparation of:

- Guidance on the Identification of Remediation Options — this guidance paper outlines how to carry out a preliminary remediation options appraisal to determine technologies that may be feasible to remediate contaminated sites. The preliminary remediation options appraisal forms the first stage of a remediation action plan (RAP).
- Application Guides for various technologies — these provide guidance on the practical application of particular technologies for the treatment of contaminated soil and groundwater. Information is included on the important factors that need to be considered when planning and preparing a Remediation Action Plan, and whether treatability trials will need to be carried out. The Application Guides provide guidance on the following:
    - Soil
        - Containment.
        - Chemical immobilisation and solidification.
        - Bioremediation.
        - Soil washing.
        - Thermal desorption.
        - Excavation (and disposal).
    - Groundwater:
        - In Situ Air Sparging.
        - In Situ Chemical Oxidation (and surfactant enhanced in situ chemical oxidation).
        - Skimming systems.
        - Monitored natural attenuation.
        - Barrier systems (permeable reactive barriers and cut off walls).
        - Pump and treat.
    - Vapour:
        - Soil vapour extraction.

THE INFLUENCE OF CLIMATIC UNCERTAINTY ON GROUNDWATER RESTORATION AND WATER RESOURCE PROTECTION

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INTRODUCTION

The manifestation of shifting climatic conditions, both short term and long term, will have a strong influence on the design of reliable and protective groundwater contamination mitigation and water resource protection measures. Forecasts of our hydraulic future cannot as easily rely on historical patterns. In many parts of North America, Australia, South America, and Europe precipitation and runoff patterns are changing and extreme climatic events (droughts, storms, floods) are expected to become more frequent. Rising temperatures and sea levels are being observed and are forecast to become more prevalent. These anticipated conditions relate strongly to water resource availability, distribution, and vulnerability, and they challenge our ability to develop effective and robust contaminant clean up and long-term and reliable protection measures. Likely perturbations to groundwater level and flow conditions must be assessed; groundwater remediation measures must account for the uncertainty in near shore and continental recharge conditions; and, the fate of contaminant plumes will arguably become less predictable as climatic variability affects both hydraulic and chemical conditions in the subsurface.

DISCUSSION

The convention of assessing and designing "30-year" groundwater protection and clean up remedies may not be as reasonable given the rapidly changing considerations in hydraulic conditions in some geographic areas. Similar to adaptive strategies that are becoming considered for shoreline environments in the face of sea level rise, for example, a reality is that our remedial strategies could also benefit from adaptive approaches for designing and implementing both passive and active restoration concepts. This will require a better understanding of how our remedial systems age, either acutely or chronically, with changing hydraulic conditions, and how we can engineer and monitor remedial systems using reliability-based methods under different hydraulic scenarios. Example projects in the northern U.S., such as an aquiculture protection project near an active iron mining area requires consideration of long-term climate changes for developing a passive groundwater treatment system; and consideration of the impact of groundwater pumping for water use near active remediation areas in arid lands require consideration of how this pumping will impact sensitive ecological areas if more pumping due to drought is necessary.

While climatic and hydrologic changes demand consideration of technical innovations to promote reliable and protective water resource clean up measures, consideration of key stressors are important for designing an economic model for which decisions on which measure may be most defensible for a given situation. Theses stressors will include toxicological changes for given chemicals as geochemical conditions (e.g., aerobic or anaerobic) in a groundwater system as hydraulic shift; and may include usability of groundwater depending on the availability of surface water in drought conditions or in periods of rapid urbanization. Environmental stresses can increase due to climatic stress, and the resulting impact on consumer goods, agriculture, and ecosystem needs (Figure 1) will provide even greater stress on the distribution of water resources, which will impact the magnitude of the economic investment into a groundwater cleanup method. The economic consideration is important to assuring that that the groundwater resource remains a viable

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asset as determined by both environmental and economic net benefit analysis for the myriad of environmental and human uses of a given water resource.

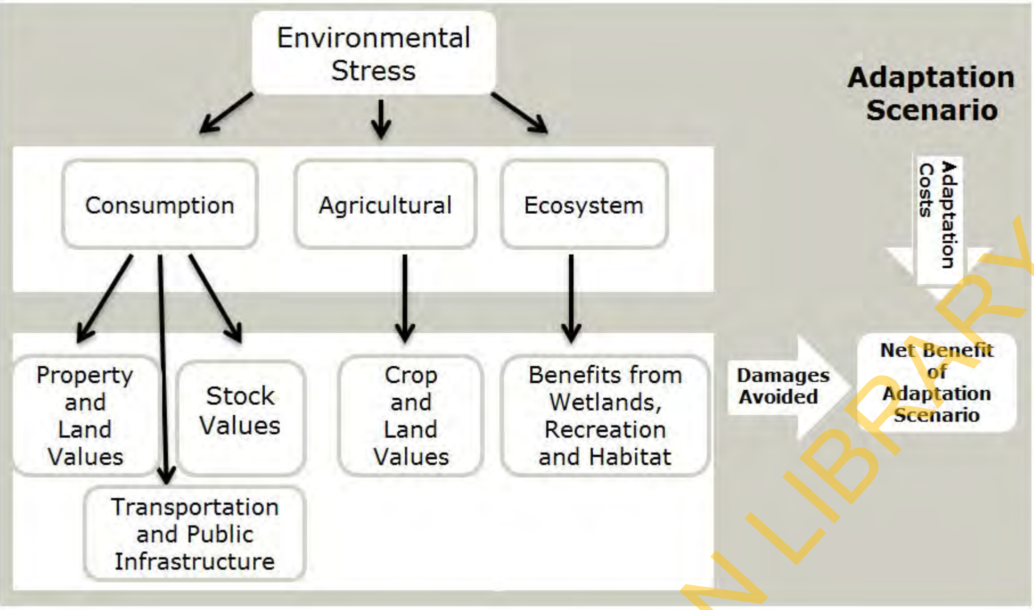

Fig. 1. Incorporating Economics to Climate Change and Water Resource Stress Adaptation Management.

CONCLUSIONS

Over the past several decades, the design of remedial measures for chemically-affected groundwater has evolved from conventional removal actions (e.g., pump and treat), to hydraulically passive biological methods (e.g., bioremediation) as influenced by advances in technological understanding of both engineering methods and the chemical characteristics of contaminants, as well as innovative site characterization methods. These approaches principally, however, have been based on application to relatively stable hydraulic conditions for the subject sites. With the general acceptance that changing climatic conditions are strongly influencing hydraulic characteristics and that past conditions may no longer be as reliable a predictor of future conditions, a new paradigm of remedial design considerations for contaminant clean up and groundwater protection will ensue. Examples will be used for demonstration and discussion during this presentation.

SEA LEVEL RISE AND CONTAMINATED SITES — MORE CHALLENGES AND HARD DECISIONS LIE AHEAD

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INTRODUCTION

Investigating and cleaning up contaminated sites is often challenging at the best of times. Sea level rise will add further scientific, technical and regulatory complexity which will need to be addressed sooner than many realise, long before predicted inundation of these sites occurs.

There are many potentially contaminating industries and land uses located on coastal and estuarine shores that will increasingly experience flooding during storms, regular tidal flooding and eventually complete inundation in the decades ahead. Permanently submerged land will become part of the marine environment and therefore likely to require more stringent cleanup standards than need to be met now. Achieving this is likely to incur greater investigation and remediation costs, especially if action is delayed until sea levels, and adjacent groundwater levels, have risen further.

NOT A SMALL PROBLEM

In the context of the current projections of average global sea level rise, studies of the Australian coastline have shown that thousands of residential, commercial and industrial properties are at risk. In addition there are many old landfill sites in vulnerable locations that will be affected. When our understanding of potential contaminated sites and the current costs of investigation and remediation are considered, there are billions of dollars of potential liability for home and property owners, property occupiers, financial stakeholders and all levels of Government.

THIS IS GOING TO BE DIFFICULT

Current policy and regulatory frameworks in Australia are not developed to cope with this consequence of climate change. The issues for all the stakeholders are complex and difficult. It is likely to take many years to develop the policies and regulatory framework across the many jurisdictions.

MANY UNANSWERED QUESTIONS

There are many questions to be addressed. Here are some examples:

(a) The responsible parties did not choose the ‘future land use’ so why should they pay for added costs to meet the more stringent cleanup criteria that may be required for marine ecological conditions? Should they be compensated, and if so, by whom?

(b) Does the hierarchy of responsibility enshrined in current contaminated sites legislation still apply?

(c) What happens if the responsible party cannot pay and the liabilities default to the banks or to Government?

(d) Who will pay when property values drop in vulnerable areas as it becomes even more indisputable that inundation from sea level rise is going to happen and cost recovery cannot be achieved from the resale of the remediated property?

(e) Should adaptation include legal instruments to empower Government to order mandatory relocation from vulnerable premises? All of the infrastructure may need to be demolished and removed on the properties in the affected areas so that contamination investigation and remediation can occur in time? What does ‘in time’ mean?

(f) Should there be a national approach to policy and regulation?
(g) What if we do nothing?

If the rate of global average sea level rise continues to increase, as it has done for the past 20 years, then answers will be needed within the next decade. The Australian experience in the development of the contaminated sites legislation in the States and Territories, and the more recent revision of the NEPM for contaminated sites investigation, shows that years will be required to address the issues. In the meantime, sea level rise will not wait.

SUMMARY

The rate of global average sea level rise is increasing due to anthropogenic climate change. The rate has accelerated in the past 20 years and climate scientists expect further acceleration in the coming decades. Thousands of residential, commercial and industrial properties are at risk of increased flooding and eventual inundation. The inescapable, and involuntary, change of land use to a marine environment, and how the transition is to be managed poses substantial financial risk to the stakeholders involved.

Major challenges and hard decisions lie ahead for the community, policy makers, land owners / occupiers, banks, the legal profession and all levels of Government. The answers to some of the difficult issues will be challenging and disturbing to some stakeholders, yet they must be addressed to allow for strategic planning. This presentation will discuss some of issues further and present suggestions on the path forward for consideration.

GROUNDWATER MONITORING & REMEDIATION UNDER CHANGING CLIMATE CONDITIONS

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INTRODUCTION

At contaminated sites, groundwater monitoring and remediation systems are implemented to monitor conditions and to control or reduce risks to potential receptors. These systems are designed based on site-specific groundwater monitoring data and, at many sites, may be operational over several decades. When timeframes extend to decades or longer, the effects of climate variability and climate change (e.g. Barron et al., 2011; Steffan et al., 2013) on monitoring, remediation, and the risk assessment that underpins their design should be considered explicitly. At most sites, the data and conceptual site models from which we assess risk and develop monitoring or remediation programs are limited. They may not encompass more extreme conditions such as drought or flood and tend to be based on shorter term, potentially "average" climate conditions. Consequently they may not represent the longer term variability (such as el Niño/la Niña weather patterns) or conditions resulting from extreme events, which may alter significantly the effectiveness of monitoring and/or remediation programs.

BACKGROUND

At several sites the period over which monitoring or remediation has occurred has included a change in environmental conditions (most typically changes in rainfall patterns). Examples include changes to the water table depth in response to development of or breaking drought conditions or flooding, and changes to groundwater flow directions as recharge and discharge zones change. At several of these sites this has led to:

- Re-evaluating the extent to which contaminants are delineated and stable as water levels and groundwater flow directions change;
- Reassessing the extent to which all potential receptors have been identified, particularly where the water table has risen, or groundwater flow directions have changed;
- Reassessing potential risks associated with contaminants in groundwater and/or vapours due to changing conditions and receptors;
- Modifying the groundwater monitoring program (frequency, locations, parameters) to monitor changed conditions; and in some cases
- Modification or redesign of groundwater remediation systems to control contaminant transport and manage risk under changed water levels and groundwater flow directions.

For facilities such as a landfills or tailings/waste rock impoundments, that have design lives of at least several decades and which are integral to remediation strategies, the effects of climate variability and climate change need to be considered explicitly in the design and throughout monitoring.

RESULTS AND DISCUSSION

In southeastern Australia, when the >10 year drought of the early 2000s broke in 2010, water levels rose and groundwater flow directions changed as dormant recharge areas were reactivated. These led to the following effects at several sites where monitoring and/or remediation were being undertaken:

- Increased concentrations of dissolved phase hydrocarbon in groundwater as the water table rose and mobilised hydrocarbons from the capillary fringe;
- Apparent “disappearance” of LNAPL from wells and reduction in effectiveness of LNAPL skimming as well screens were submerged beneath the water table;
- Identification of new/different receptors and lack of plume delineation as groundwater flow directions changed with changing recharge areas.

Extreme weather effects such as the Queensland floods in 2011 posed similar challenges for groundwater monitoring, risk assessment and remediation, and led to a sustained rise of the water table by over 10 m. Under these conditions, vapour intrusion away from the source area, not previously considered because of the depth to the water table, became a potential exposure pathway that required assessment.

CONCLUSIONS

The changing climate conditions that we are experiencing in Australia require us to think beyond the short-term data sets on which we typically base monitoring and remediation design decisions. Particularly in the case of recalcitrant contaminants such as chlorinated hydrocarbons or metals where groundwater contamination may persist for decades, and at facilities with extended design lives, we need to consider effects of future changes in weather and climate conditions on monitoring and remediation system performance and design.

Groundwater monitoring programs need to be adaptive and flexible to facilitate the identification and recognition of changing conditions. This will allow risk profiles to be reassessed and remediation strategies re-evaluated to address risks. Groundwater remediation designs need to be designed to allow for effective performance outside of the “current” data, recognising the potential for water levels to change in response to changing climate conditions.

REFERENCES

Barron, OV et al., 2011. Climate change impact on groundwater resources in Australia, Waterlines report, National Water Commission, Canberra.

Steffen, W, Hughes, L and Karoly D, 2013. The Critical Decade: Extreme Weather. Climate Commission Secretariat, Commonwealth of Australia (Department of Industry, Innovation, Climate Change, Science, Research and Tertiary Educations), Canberra.

IMPLICATIONS OF CLIMATE CHANGE FOR SITE ASSESSMENT, MANAGEMENT AND REMEDIATION

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BACKGROUND

Ramboll) Environ (is rapidly expanding its capabilities in climate adaptation in Australia and globally to help clients considering future climate impacts when planning or designing cities and new infrastructure or making strategic decisions with long-lasting implications. There is a need to ensure that these decisions can cope with or take account of the projected climate over the applicable life span. The challenges this poses for all environment and sustainability professionals involved in contaminated site assessment, management and remediation is outlined in this paper. Despite the complexity and urgency of this task there is as yet very limited research that has been undertaken to guide site assessment specialists.

Public infrastructure and decision-making internationally requires for its planning, design, delivery, operation and maintenance that minimum acceptable requirements ('what to do') are followed, these are set out in the many thousands of formal Australian and international standards, developed by Standards Australia and its international counterparts. The standards are complemented by numerous industry-developed 'how to' guidelines that provide more detailed advice on current best practice for specific types of infrastructure. Unfortunately, at present only a handful of standards explicitly for consider of climate change impacts (direct, indirect and/or flow-on) and provide for the design to make adequate provision to handle such impacts. Moreover, because the standards specify the minimum legally acceptable design requirements, doing more than what the standard requires (such as considering possible climate change impacts) is currently discretionary. As such, that can only happen when the infrastructure owner or purchaser agrees to bear the additional time and cost involved on the basis of arguments set out in a business case.

In a similar way site assessment and management processes are guided by standards, guidelines and specifications. And similarly unfortunately, at present none of these explicitly consider a future changed climate and its impacts (direct, indirect and/or flow-on) nor is there consideration for the site design decisions to make adequate provision to handle such impacts. More and more professional areas are identifying this as a major issue faced by those responsible for the design, construction or ongoing management of long lifetime projects. The issue is that most engineering and other standards, technical specifications, guidelines etc. are backward looking. They document best practice based on what has been found to work well in the past and in historical climate conditions. That approach has served human society very well until quite recently, and under a stationary climate would remain an eminently sensible approach.

WHO IS CONSIDERING CLIMATE CHANGE?

There is therefore a growing number of companies and governments (at all levels) that are considering future climate and taking steps to make cities, organisations, infrastructure and strategic decision making more climate resilient. Ramboll Environ understands this need and the key questions clients are seeking answers to, such as:

- What is the extent of climate risk, including timing, thresholds, interdependencies, triggers and limits?
- What are the priority areas or hotspots for detailed assessment and treatment?
- How effective are existing controls?
- What opportunities exist for us in responding to a changing climate?

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TOOLS AND INFORMATION TO ASSIST IN CONSIDERING FUTURE CLIMATE

This presentation will walk clean-up professionals through the stages of a climate risk assessment highlighting available information and guidelines to assist practitioners in considering future climate and its potential impact upon a site.

CLIMATE AND SITE REMEDIATION

The climatic conditions, both short term and long term, can have a strong influence on the design of reliable and protective site remediation measures. Forecasts of site conditions cannot as easily rely on historical patterns. Climate modelling is now available to practitioners of future precipitation and runoff patterns and frequency, duration and intensity of future extreme climatic events (droughts, storms, floods). Rising temperatures and sea levels can also be forecast. These anticipated conditions do not just relate to water resource availability, they also relate to site stability and as such may challenge our ability to develop effective and robust contaminant clean up measures. The conventions of assessing and designing site remedies without reverence to new and emerging future climate data needs to be challenged and the new reality is that remedial strategies could benefit from adaptive approaches. The following site contamination and remediation practices are sensitive to climatic conditions and therefore need to consider future rather than historical climate conditions:

- Perturbations to groundwater levels and flow conditions.
- Remediation measures selection, sensitivity to extreme conditions.
- Near shore and continental recharge conditions.
- Contaminant plume predictions (fate and transport modelling).
- Hydraulic and chemical subsurface conditions.
- Moisture content of soils and evaporation rates potentially impacting dust including asbestos.
- Vapour intrusion rates.
- Sea level rise and storm surge inundation and flooding of coastal gully fill.
- Infiltration modelling and leaching of contaminants under intense rainfall events.
- Stability of containment cells such as surface erosion.
- Capping methods sensitivity to shrinkage and intense rainfall.
- Phyto-toxicity with changing species.

CONCLUSIONS

There are now available downscaled and ‘fit for purpose’ climate projections available to site practitioners. There are also many step by step guidelines for climate risk assessments. It will be imperative for or all environment professionals involved in contaminated site assessment, management and remediation to embed future climate considerations in their work.

CONTAMINATED LAND: SCIENCE, GOVERNMENT AND THE MARKET — SQUARING THE CIRCLE IN BOTH HEMISPHERES

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Contaminated land and groundwater present significant challenges to those charged with environment and human health protection and economic development and renewal. Their successful remediation represents research and development as well as economic, environmental and social improvement opportunities.

Many jurisdictions have wrestled with tackling soil and groundwater contamination – both its prevention, identification, assessment and treatment. This paper focuses on experience in Scotland and South Australia where thousands of hectares of contamination has been broadly identified in thousands of sites and places this in a general context.

Often we look to the US for guidance, given their experience in the context of industrial pollution, the development of EPA standards and the use of the Superfund mechanism. US and UK best practice are commonly cited. Australia too has developed a relevant NEPM. Scotland first undertook an audit of vacant and derelict land and began to construct a register in 1988, with annual updates undertaken since 1993, increasingly seeking to identify contamination. It has developed experience of the management and renewal of sites with radioactive, heavy metal and other toxic contamination since the late '70s and the statutory regime is 25 years old. The regeneration and decontamination of significant areas has often been led by Government, with partnerships of economic development and environment agencies, local government and private partners for at least 40 years and most recently the Commonwealth Games in Glasgow presented a great opportunity for remediation and transformation. There are currently c 11000ha identified in c 3000 sites. In South Australia the rather more sophisticated and robust legislative regime is 22 years old and has been increasingly refined over time. Its audit system and register approach offer real potential to target and manage risk and improvement. There are officially over 1000 sites and the area of actual contamination is unknown. There is no reason to believe it is less than thousands of ha. Extensive mining areas and mining methods – heap leaching etc. – reinforce that assumption. In both domains both the records of industrial activity and contamination data quality are relatively poor.

The actual physical challenge of assessment and remediation can be made even harder by a number of factors. These include an insufficiently robust and integrated planning and development system; cultural issues; and especially the concomitant financial and political constraints when scientific or market realities are not understood or are overly simplistically considered. In some operating environments the task of tackling industrial contamination and histories of bad pollution, waste management and development practice is made harder by a lack of capacity and capability. Public servants, developers and politicians may be unable to understand basic scientific information. They may lack the political will or make available inadequate resources to take the threat to habitats and communities seriously. Some politicians see only the need for development and homes or new industry at minimal costs and without controversy, ignoring, failing to understand, or simply fearing the realities of situations over which they or their predecessors may have presided.

Persistent and pernicious pollutants have to be contained, treated and removed, ideally they should of course be prevented….but radioactive materials, chlorinated hydrocarbons, heavy metals, asbestos, biologically active agents etc. have all been allowed to enter and remain in environments, often unseen and unnoticed, until the ground is disturbed, water table is tapped, new infrastructure is involved or a health scare emerges.

Dealing with contamination is often viewed as a problem. It may not be viewed as a public policy or political priority like healthcare, education and policing and hence is underinvested in – both in prevention and remediation terms. Planners often give the go-ahead, including under political pressure, to the building of new homes in locations adjacent to former industrial sites and sometimes even on former sites, often because the appropriate information is not known or shared intelligently in advance and the developer might not be aware of what they are getting in to. Developers may receive support for the extra costs of developing “brown field” sites because of the market failure and hence also avoid protected or sensitive green locations. But they may also be under pressure to deliver results and meantime fail to assess costs, treatment and disposal issues, risks, consequences and other difficulties adequately. Properly cleaned up, dealing with contamination is an excellent, socially desirable outcome. Badly done, it’s a ticking bomb for these future residents and society at large, especially where the public may be the funder of last resort and polluters or poor developers may walk away from liabilities. Those pointing out the challenges or risks or necessary thorough approach may also be viewed as being over-sensitive, NIMBYs, anti-development, even anti economy and so, vilified or marginalised, they may fall silent.

Tackling contamination, in Australia, in Europe and worldwide requires understanding of the historic inputs – their chemical, physical and biological qualities and the quantum, source and timetable of events as well as an appreciation of the receiving environment, the contiguity of the soil, water and geological structures involved, the context surrounding the site – other land uses, the presence of wells etc. and the use to which the site and its environs will be put subsequently. The diagnosis of what is present, possible and to be done as well as the actual design and delivery of a solution has many facets. These include: the Law, good policy and practice, the planning system, engagement with community needs and expectations, the market economics and public investments necessary etc. to build a full picture of the scope for particular after-use outcomes as well as the remediation and construction methods, management of wastes, containment of the site and its underlying hydrogeology and then appropriate and credible implementation bodies and contractors as well as regulators, and the arrangements for protection of workers, residents and others involved in the location. It is a long checklist. It is often not an issue amenable to quick or cheap fixes, however keen a politician or developer might be to be photographed at the topping out or commissioning. But done well, as in benchmark examples of good practice worldwide, it can result in the positive and catalytic transformation of cities and communities for the long term. Rotterdam, Glasgow, London, Sydney and many other cities boast stories of dramatic improvement.

Examples of good and bad policy and good and bad outcomes from both hemispheres will be used to show what can be achieved and how to avoid the worst excesses of market and implementation failures. A case for expert input and an integrated approach to managing these issues is suggested.

SUBSURFACE CHARACTERISATION, MODELLING, MONITORING, AND REMEDIATION OF FRACTURED ROCKS

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BACKGROUND/OBJECTIVES

Geological and geotechnical characterising, modelling, and monitoring of the subsurface are integral to safe, economical, and responsible development, maintenance, operation, remediation, and decommissioning of infrastructure related to energy, water, waste, and transportation. Modelling and monitoring fluid travel paths and velocities through subsurface fractures and matrix are among the most significant engineering challenges associated with these tasks. A committee of the National Research Council has conducted a study to address issues relevant to subsurface flow and contaminant transport in fractured media, including low permeability and low porosity media, as well as in deep (3 to 5 kilometres) fracture systems. Subsurface characterisation, modelling, monitoring, and remediation (SCMMR) issues applicable throughout the lifecycle of engineered facilities that have the potential to release contaminants and pose risk to groundwater quality have been considered.

APPROACH/ACTIVITIES

As part of its information gathering, the committee convened a workshop to examine the state-of-art and state-of-practice in:

- Subsurface fracture and matrix characterisation, especially relevant geotechnical, hydrological, and geochemical properties, and the development of conceptual models;
- Detection of fluid and contaminant pathways and travel times;
- Detection and modelling of factors that affect changes in geotechnical and hydrological properties over time (e.g., decades to millennium), including thermal, hydrological, chemical, and mechanical (THCM) processes;
- Groundwater and contaminant transport modelling, monitoring, and remediation, and how these can aid decision making during facility design, operation, remediation, and decommissioning;
- Early indicators (such as change in fracture properties, moisture levels, background chemistry) of system failures resulting in unintentional release of fluids; and,
- Potential mitigation measures to eliminate or reduce adverse impacts of system failures and related releases to the environment.

The committee is issuing a final report in August that will include findings and conclusions with respect to (i) where research and development could improve the current state-of-art in SCMMR, and (ii) where incorporation of scientific and technical advances could enhance the state-of-practice in SCMMR and (iii) where enhanced science-based understanding could inform federal regulations, policies, and implementing guidance.

RESULTS/LESSONS LEARNED

This talk will present the overview of the finding of the committee, delivered by one of the ten committee members. The focus will be on how the state of the art has advanced over the past 20 years, present the committee's recommendations on a holistic and heuristic approach to site investigation in fractured rock, and discuss where additional research is needed to allow for effective characterisation, investigation, monitoring, and remediation at fractured rock sites.

GEOLOGICAL INVESTIGATION USING MULTIPLE LINES OF EVIDENCE TO DETERMINE LNAPL PRESENCE IN BEDROCK

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INTRODUCTION

A geological investigation (GI) comprising rock coring, dewatering trial, down-hole geophysics and Laser-Induced Fluorescence (LIF) was undertaken at fractured phyllite bedrock site, with a historical LNAPL presence.

Background

Historical investigations detected LNAPL within the fractured phyllite bedrock aquifer at a site. Remediation works including excavation, soil vapour extraction and multi-phase extraction with surfactant injections previously undertaken at the site were considered to have achieved limited success with the low hydraulic conductivity bedrock limiting LNAPL and dissolved-phase recovery.

LNAPL was not detected in 2014, but inferred through elevated dissolved-phase concentrations. A highly fluctuating groundwater table was potentially masking LNAPL presence. Historically, investigations in bedrock structure (fracture sizes, preferential pathways, weathering) and LNAPL recoverability had not been undertaken.

Objectives

The objectives of the GI were to:

(a) To investigate the on-site subsurface geological conditions, including weathering, the presence and nature of fractures and potential preferential groundwater flow pathways within the subsurface.

(b) To investigate whether LNAPL was present in the subsurface and its location and potential flow pathways within the geology.

(c) Investigate whether subsurface LNAPL is residual or recoverable.

FIELDWORK METHODOLOGY

Field work was conducted in three stages: drilling; dewatering trial, downhole geophysics, backfilling and LIF.

Drilling

Three boreholes (BH1 to BH3) were drilled using sonic drilling with PID field screening undertaken on the recovered core and geological characterisations logged. Based on PID readings samples of core were submitted for soil and crushed rock analysis.

Dewatering Trial

Following drilling, a dewatering trial was conducted at each of the boreholes to determine if lowering the water table would induce LNAPL flow into the boreholes. A submersible pump lowered the water table to approximately one metre below the depth of hydrocarbon impact noted in the core during drilling. Drawdown was maintained for 2.5 hours.

Groundwater samples were collected prior to, periodically throughout and 2.5 hours after cessation of the pumping trial. Samples were visually assessed for sheen/LNAPL and were field screened using a PID. Samples were submitted for laboratory TPH/BTEXN analysis.

Downhole Geophysics

Downhole geophysics were subsequently undertaken at each borehole comprising: optical televiewer, acoustic televiewer, three arm caliper and fluid temperature and conductivity probe.

Backfilling and LIF Works

One week prior to LIF works, each of the three boreholes were backfilled to ground surface with a mix of organoclay and 16/30 graded sand. The combination of sand and organoclay was intended to provide sufficient permeability for LNAPL/dissolved hydrocarbon to penetrate the borehole, but also promote discrete sorption of the hydrocarbon and inhibit its vertical migration.

A LIF probe was advanced at each backfilled borehole (BH1 to BH3) using a direct push Geoprobe™ drill rig.

RESULTS AND DISCUSSION

Geology and Downhole Geophysics

Bedrock was noted as consolidated phyllite with tight horizontal foliations, clay infilling in fractures and quartz veins up to 20mm. Weathering generally decreased with depth, with decomposed bedrock recovered as clay observed to be most prominent within the top 3m of the boreholes. Elevated PID readings and hydrocarbon odours were identified within the decomposed clay zones and clay infill, with no staining, odour or elevated PID readings recorded within the rock samples. TRH/BTEXN concentrations were generally below limit of reporting for all rock samples and all but two soil samples.

Dewatering Trial

No LNAPL/sheen was observed in the effluent or samples during dewatering. PID readings measured recorded up to 76ppm during recovery phase monitoring at borehole BH1. Groundwater results showed increase of TRH and BTEXN concentrations in BH1 and BH3 during dewatering. Concentrations increased further during recovery at borehole BH1.

LIF

Maximum % of relative emitter (RE) ranged between 2.8% (BH2) to 5.6% (BH3). These relatively low results indicated that LNAPL migration into the backfilled boreholes was unlikely to have occurred.

A LIF spike recorded at 4.25mbgl in BH3 correlated to a fracture observed at the same depth in the optical televiewer and in the sonic core sample within a zone of moderate hydrocarbon impact. Though the magnitude of the spike was insufficient to suggest LNAPL, it corresponded to a narrow discrete depth interval and stood out relative to the baseline response of the instrument, suggesting subtle and discrete hydrocarbon migration into the borehole at this depth and location.

CONCLUSIONS

The phyllite bedrock comprised consolidated, highly foliated bedrock with quartz veins and fractures generally filled with clay. While a LIF profiling indicated a subtle spike in BH3 at 4.25m, no LNAPL/sheens were reported during the GI. Correlated with the lack of LNAPL inflow from the dewatering trial, it is inferred that LNAPL at the boreholes investigated was either not present or adsorbed to the clay material within the subsurface and not mobile.

Based on the observations of the works, it was inferred that while increases in dissolved-phase concentrations were noted, groundwater extractions methods would unlikely be effective in removing LNAPL.

DEVELOPING CONCEPTUAL SITE MODELS FOR THE INVESTIGATION AND REMEDIATION OF FRACTURED ROCK

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INTRODUCTION

It is widely recognized that the investigation and remediation of fractured rock sites presents significant challenges for geoscientists and engineers worldwide. Deployment of effective remediation at fractured rock sites requires representative conceptual site models (CSMs) that describe the characteristics of the flow domain and the physics of fluid flow at multiple spatial and temporal scales (Faybishenko et al. 2000). Here we critique current methods to characterize fractured rock, based on process-based understanding of the physical limitations to implementing specific remedies in fractured rock. Data requirements to develop process-based CSMs are presented for exemplar fractured rock environments, including basalt, sandstone and limestone. We discuss what the industry needs to know, where to access the information (best-practice guidance, international standards, peer-reviewed literature) and present recommendations for developing CSMs to support successful site closure at fractured rock sites.

BACKGROUND

Fluid flow in fracture networks is dependent on the extent to which individual fractures, and fracture sets, are connected. Although understanding of the connectivity of fracture networks is of critical importance in predicting contaminant transport, quantification of the extent of connectivity is typically uncertain when fractures are observed only at the boreholes scale. Outcrop analogues, which are the surface expression of equivalent fractures systems at depth, are frequently not available to the investigator, which results in an incomplete description of the interconnectivity of fractures and fracture sets. Predicting contaminant transport and fate in fractured rock demands detailed understanding of preferential flow paths, which occur in discrete fractures that represent a subset of the physically connected fracture system. Hydraulic tests and tracers tests, deployed to discriminate fluid flow in fracture systems, demand the adoption of test methods that accommodate contrasts in hydraulic conductivities between the fractures (transport domain) and matrix (storage domain). The contrasts in hydraulic properties between transport and flow domains may be extreme and localized, and may vary over 6 or more orders of magnitude. The following section considers the characterization of fractured rock sites, outlines process understanding required to describe contaminant transport and fate in fractured rock systems, and discusses data requirements to develop advanced CSMs for the selection, implementation and performance assessment of remediation technologies.

SITE CHARACTERIZATION OF FRACTURED ROCK

Fracture network characterization involves reconstruction of the structural controls on fracture evolution, generic description of the characteristics of fracture sets and more specific description of individual fractures, and the quantification of the extent of connectivity of the physical fracture system.

Developing robust and defensible CSMs of groundwater flow and contaminant transport and fate in fractured rock builds on the reconstruction of the physical fracture system and proceeds with a description of the location and orientation of specific fractures, fracture size (areal extent) and aperture, porosity and permeability of the rock matrix, hydraulic head throughout the system, inflow and outflows of groundwater, and the chemical interactions between contaminants in the transport (fracture) and storage (matrix) domains (Witherspoon, et al., 1987; Schmelling and Ross, 1989).

At fractured rock sites impacted by non-aqueous phase liquids (NAPLs), the prediction of contaminant transport is further complicated by the physicochemical properties of immiscible fluids, including density, viscosity and interfacial tension (Kueper and McWhorter, 1991). Much attention has been given in the literature to the development of more representative CSMs at sites where NAPLs can be recovered, and analysed for physical properties and chemical composition. Examples of a range of fractured rock systems are presented to describe fracture network controls on fluid flow and understand density and capillary effects on NAPL migration.

The use of published literature to develop the initial CSM and constrain estimates of flow and transport in fractured rock is discussed and contrasted with subsequent iterations of the CSM based on site-specific measurements. The availability and limitations of site investigation tools for fractured rock sites will be discussed.

SUMMARY AND RECOMMENDATIONS

The inherent complexity of flow through fractured rock, which is typically characterized by double porosity and dual permeability, continues to challenge remediation engineers. Developing representative and defensible CSMs of fractured rock demands a suite of site investigation tools that adequately describe both transport and storage domains.

Comprehensive site characterization is considered to provide a complete description of system behaviour in fractured rock. However, limitations in our ability to accurately represent site-specific features suggests that site characterization objectives should be driven by understanding how much needs to be known about the fractured rock to predict the future behaviour of the system. For remediation in fractured rock this means knowing what questions are reasonable to ask, rather than oversimplifying the entire system in an attempt to answer all questions.

Implementing successful remedies in fractured rock requires expertise in high-resolution site characterization tools, adoption of best practice guidance, and knowledge transfer from leading practitioners and researchers. R ecommendations are presented for the development of advanced CSMs for the remediation of fractured rock by reference to current research, presentation of case studies, and discussion of lessons learned from related disciplines including detailed studies of the investigation of deep repositories for radioactive waste disposal.

REFERENCES

Faybishenko, B., C. Doughty, M. Steiger, J. C. S. Long, T. R. Wood, J. S. Jacobsen, J. Lore, and P. T. Zawislanski (2000), Conceptual model of the geometry and physics of water flow in a fractured basalt vadose zone, Water Resources Resesearch, 36(12), 3499–3520, doi:10.1029/2000WR900144.

Kueper, B.H. and McWhorter, D.B., 1991. The behavior of dense, non-aqueous phase liquids in fractured clay and rock. Journal of Ground Water, Vol. 29, No. 5, pages 716–728

Schmelling, S. G. and R. R. Ross, 1989, Contaminant transport in fractured media: models for decision makers. EPA Superfund Issue Paper. EPA/540/4-89/004.

Witherspoon, P.A., J.C.S. Long, E.L. Majer, and L.R. Myer. 1987. A New Seismic-Hydraulic Approach to Modeling Flow in Fractured Rocks. In Proceedings, NWWA/IGWMC Conference on Solving Ground-water Problems with Models, Denver, CO, February, 10-12, 1987; National Water Well Assn., Dublin, Ohio.

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FRACTURED NEWER VOLCANIC BASALT – UNDERSTANDING KEY PROPERTIES THAT INFLUENCE REMEDIATION EFFICACY

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INTRODUCTION

The variable weathering of the Newer Volcanic basalt (basalt) can present challenges to the implementation and effectiveness of in situ groundwater remediation technologies. Often this is attributed to macro–scale features such as fracturing of the basalt and presence of clayey palaeosols which are observable from drill cuttings and rock core. This paper draws on remediation based investigations and trials that have occurred at two sites (Site A and Site B) to assess the implementation of in situ technologies such as thermal desorption, chemical oxidation and enhanced bioremediation to treat chlorinated organics in groundwater. The objective is to communicate these findings to aid in the overall understanding of various properties of the basalt rock and their implications for remediation technology selection and implementation.

BACKGROUND / METHODS

Methods supporting the development and implementation of in situ remediation technologies in the basalt include (1) laboratory analysis of total organic carbon in the rock mass and the interstitial faces of fractures; (2) column leaching tests to measure sorption and retardation properties; (3) column and batch tests to assess thermal desorption and residual mass post treatment; and (4) geochemical analysis to evaluate possible cause(s) of precipitation during chemical oxidation.

RESULTS AND DISCUSSION

Fracturing and fracture mineralogy at the micro scale

The porosity in slices of vesicular rock ranged up to 20% in Site A. There was no evidence that voids due to vesicles formed a continuous pathway, except where intersected by fractures. In massive rock slices, porosity ranged from 0% to 8% and there was evidence of fine fractures that were connected in the slice (Fig. 1). These fractures may play a role in contaminant sorption and back diffusion which can be problematic for in situ remediation.

Quantitative XRD of a fracture zone with low to moderate vesicularity from Site B indicated that primary olivine had been replaced by smectite clay, comprising about 15% of the rock mass, thereby altering the porosity and sorption characteristics of the fractured zone.

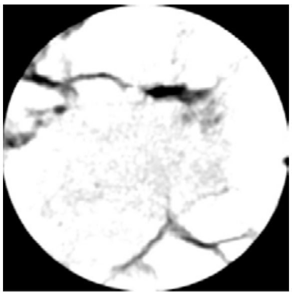

Fig. 1. CT scan of micro scale fracture in a massive basalt rock slice (83 mm diameter)

Total Organic Carbon Content & Retardation

Measured particle densities of rock cores from Site A ranged from 2677 kg m^{-3} to 2819 kg m^{-3} with a mean of 2744 kg m^{-3}. Total organic carbon (TOC) content was approximately 0.09% (range 0.07% to 0.13%) based on analysis of the total rock mass. In a separate study, Site B, the TOC in fracture zones of seven core samples ranged from the laboratory limit of reporting of 0.1% with three samples recording between TOC contents of 0.3% to 0.6%.

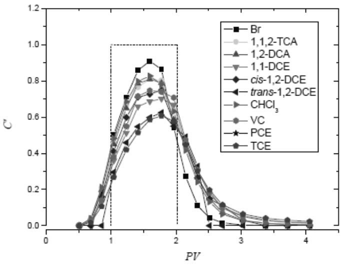

Fig. 2. Breakthrough curves of chlorinated organics – relative concentrations, column Test 2

Adsorption tests were carried out using columns packed with crushed rock from three Site A rock cores. Breakthrough curves of chlorinated organic compounds relative to Br^- indicated retardation, albeit minor, was occurring. Although there was evidence of minor differences between the sorption distribution coefficients, K_d, for individual chlorinated organics the estimated K_d values from these tests were low indicating similar results to those that might be calculated using the measured TOC. The similarity to calculated sorption coefficients suggests that there is little competitive adsorption or interference between individual chlorinated organic compounds.

The data indicate that estimating the role of adsorption based on measuring TOC in the basalt is a valid approach. However, there is the potential for higher TOC in the fracture zones where many in situ remediation reactions are likely to take place. Hence TOC in the fractures may need to be considered when estimating stoichiometric demands for treatment agents and assessing effects of desorption on long-term remediation performance.

Thermal treatment & residual sorbed mass

Packed columns of basalt rock were supplemented with a known volume of 1,1,2-TCA (DNAPL), saturated and then heated to boiling point. Subsequent leaching of the column indicated that 20% of the DNAPL remained after thermal treatment. However, about 50% of the remaining mass leached within 2.4 pore volumes and 90% within 7 pore volumes. Comparison to the results from a non treated column suggests that the thermal treatment had resulted in redistribution of the DNAPL, increasing its rate of dissolution and leaching.

Clay and rock cores from the same site were heated to 100 ^{o}C by Terratherm to evaluate mass removal efficiency (MRE). MRE's ranged from approximately 74% to 98% for a range of chlorinated organics present in the cores. These data compliment the results from the column thermal treatment trials and suggest that significant chlorinated organic contaminant mass has the potential to remain in the basalt following thermal treatment.

Chemical precipitation and cation exchange

A treatment trial involving in situ base-catalysed persulphate resulted in the formation of precipitates, identified to be calcite ($CaCO_3$) and gypsum ($CaSO_4{\cdot}2H_2O$), that potentially limited the ability to deliver the oxidant. The cation exchange capacity (CEC) and mineralogy of the rock was established to understand the potential cause of the precipitate and optimise the treatment design. The CEC of the basalt ranged from 23 meq% to 36 meq% (Fig 3). Calcium comprised 20% to 50% of the exchangeable cations, supporting the potential for formation of gypsum. The data also indicate that multiple treatments with caustic activated sodium persulphate may cause the clay minerals to swell which could also reduce the ability to deliver the oxidant. This indicates that the method of persulphate activation needs consideration to minimise precipitation and swelling of clays within the rock mass.

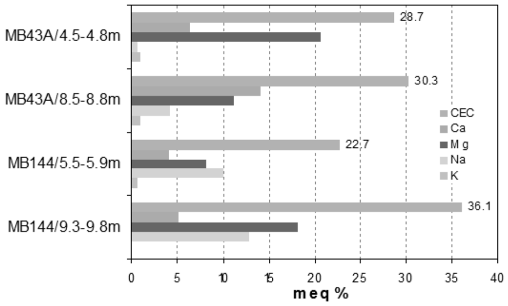

Fig. 3. Exchangeable fraction composition of basalt rock

CONCLUSION

The data from these sites demonstrate that micro-scale, physical, and chemical factors need to be considered when designing in situ treatments for contaminated groundwater in Newer Volcanic basalt. When considered with the nature of chlorinated solvents in the basalts, these factors may limit the degree of remediation that is achievable and consequently the remediation endpoints. The data to support consideration of many of these factors can be readily and cost effectively collected during site investigations.

ACKNOWLEDGEMENTS

The authors thank Orica and Dow Chemical for access to the information used in this paper.

NATURALLY OCCURRING ABIOTIC DECHLORINATION OF TCE IN ROCK MATRICES

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INTRODUCTION

Chlorinated solvents in rock matrices can serve as a long-term contaminant source in fractured bedrock aquifers, sustaining groundwater plumes for extended periods of time. The intensity and longevity of the groundwater plume will be impacted by the diffusional flux between the rock matrix and adjacent conductive fractures, as well as the fate of contaminants residing within the rock matrix itself. Naturally occurring degradation processes, particularly abiotic dechlorination processes, have hitherto not been investigated in detail to assess potential impacts on processes such as uptake into the rock matrix, and the potential for back-diffusion to sustain plumes.

METHODS

Minimally disturbed rock cores were collected from the former Naval Air Warfare Center in Trenton, NJ, USA. Initial testing was performed on rocks that were not within the TCE plume. Several different sedimentary rock types were examined. Rocks were characterized with respected to mineralogy and physical properties. Using a laboratory diffusion cell technique, a series of experiments was performed to determine the effective diffusion coefficients within the rock, as well as assessment of abiotic reaction between TCE and ferrous minerals. Subsequent experiments were performed with rock core collected from within the TCE plume to assess potential impacts of prolonged (decades) exposure of TCE on abiotic reaction. Specifically, experiments on these TCE-exposed rocks were intended to assess the capacity of the rocks to sustain any significant (with respect to diffusional flux within the matrix) rate of TCE dechlorination. First order TCE dechlorination rate constants were determined using a 1-dimensional numerical model that coupled both TCE diffusion and reaction at mineral surfaces.

RESULTS AND DISCUSSION

TCE Coupled Diffusion and Reaction in Rocks Collected Outside of the TCE Plume

Results show that diffusional flux in the rock matrix was dependent upon both the rock matrix porosity as well as bedding plane orientation. For the rock cores collected outside of the TCE plume, abiotic reaction resulting in the complete dechlorination of TCE was observed for all rock types examined. The observed reaction rate constant was proportional to the “available” ferrous content of the rock, as shown in Figure 1. Ethene, ethane, and acetylene were the observed abiotic reaction products. While the measured rates were slow compared to dechlorination rates typically considered “useful” for natural attenuation, the relative rates of dechlorination compared to diffusive flux in the rock matrix suggest that these naturally occurring abiotic dechlorination process will likely have a large impact on contaminant migration into or out of rock matrices.

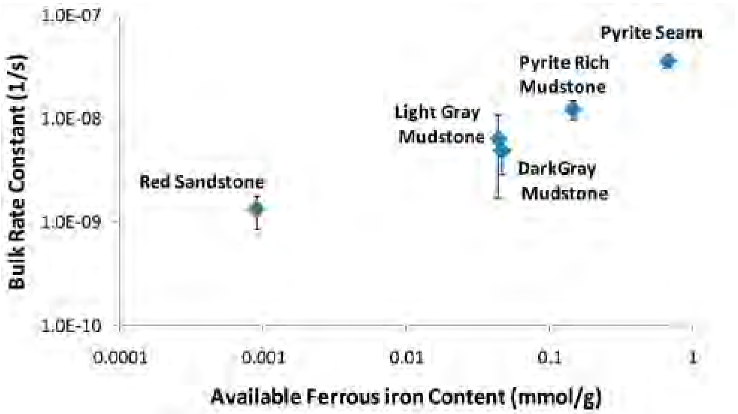

Fig. 1. Measured first-order rate constants for multiple rock types were shown to be related to the available ferrous iron content (from Schaefer et al, 2013).

TCE Coupled Diffusion and Reaction in Rocks Collected Within the TCE Plume

To determine if these processes were actually occurring *in situ*, additional testing was performed on rock core collected from within the TCE plume. Experiments using rock slices adjacent to conductive fractures (with elevated TCE concentrations in the conductive fractures) showed that abiotic dechlorination was occurring. The measured rates were similar to those measured using rocks that were not exposed to TCE, suggesting these abiotic reactions continue to occur within historic TCE bedrock plumes.

CONCLUSIONS

Overall, these results suggest that improved characterization of the rock matrix porosity and the abiotic reactivity of the matrix are important for assessing long-term contaminant fate and back-diffusion processes in bedrock aquifers. In many cases, especially for sedimentary rocks, abiotic processes may have a substantial impact on the long term fate of halogenated compounds in fractured rock aquifers.

ACKNOWLEDGEMENTS

Support for this research was provided in part by the Strategic Environmental Research and Development Program (SERDP) under Project ER-1685. We also are grateful to Pierre Lacombe Goode of the USGS for his assistance. Views, opinions, and/or findings contained in this abstract are those of the authors and should not be construed as an official US Department of Defense position or decision unless so designated by other official documentation.

REFERENCES

Schaefer, C.E., Towne, R.M., Lippincott, D.R., Lazouskaya, V., Fischer, T.B., Bishop, M.E., Dong, H., 2013 Coupled diffusion and abiotic reaction of trichloroethene in minimally disturbed rock matrices. Environ. Sci. Technol., 47, 4291-4298.

DISTRIBUTION OF VEGETABLE OIL-BASED SUBSTRATE TO REMEDIATE SHALLOW FRACTURED BEDROCK UNDER SAPROLITIC CONDITIONS

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INTRODUCTION

Successfully enhancing bioremediation of chlorinated ethenes through the addition of vegetable oil-based substrates has been problematic on some sites due to the general inability to obtain reasonably homogeneous distribution of the substrate. While attempts to increase substrate distribution by decreasing the emulsion particle size of kinetically stable emulsions have been successful predominantly in soils with higher hydraulic conductivities, the lack of stability of standard emulsions has made remediation in highly fractured bedrock and soils with lower hydraulic conductivities problematic. This has limited the use of slowly soluble substrates such as standard emulsified vegetable oil to sites with relatively homogeneous soils with moderate hydraulic conductivity. The primary goal of this project was to demonstrate the ability of a soy-based microemulsion substrate to enhance reductive dechlorination of chlorinated ethenes under saprolitic conditions and to determine the potential maximum extent of influence using standard injection point spacing.

METHODS

In order to conceptually prove that enhanced reductive dechlorination could be successful in highly permeable shallow bedrock and associated low permeability saprolitic soil above the bedrock, a thermodynamically stable soy-based microemulsion product (LactOil® soy microemulsion) was injected in a pilot test area on a site in east-central Kansas. Thermodynamically stable emulsions retain their particle size for extended periods of time when compared to poorly kinetically stable emulsions. This stability was hypothesized to be able to increase the distribution of the substrate within the system. An increase in distribution would lead to an increase in the radius of influence which would not only reduce the number of injection points required to treat a site but would also help ensure better distribution of the substrate between injection points.

The subject site is generally characterized as including saprolitic soils of varying thickness ranging from several feet to about 12 feet grading from very low permeability soils near the surface to a highly permeable limestone unit followed by shale bedrock. The upper soils consist of about 58% silt, 40% clay, and 2% sand. The limestone unit below the upper soils follows the general surface topography but “pinches out” near the downgradient end of the site. The limestone unit is thought to be the primary pathway for shallow groundwater. Both the limestone unit and overlying soils exhibit very low yield.

The original plume was estimated to include a surface footprint of about 30,000 square feet with a vertical treatment horizon of 10 feet. Based on an empirical method of determining the substrate dosage it was estimated that 16,650 pounds of substrate would be required to address the entire plume. Since this pilot test was intended to demonstrate the viability of using enhanced bioremediation to address this site, only 4,950 pounds of material were injected into areas of the plume where the concentrations of monitoring wells were more predominant. Although the treatment was expected to show results in the immediate areas where monitoring wells were concentrated, the wells in the remainder of the plume were to be used if possible to indicate the maximum extent of influence of the substrate.

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RESULTS AND DISCUSSION

Data collected over a period of nine months after application of the microemulsion showed a decrease of chlorinated ethenes in two of four monitoring wells from over 1,000 ug/L total chlorinated ethenes to non-detectable levels. The remaining two wells showed decreases in total ethenes ranging from 34% to 89%. Table 1 presents representative chlorinated solvent concentration data over a period of 9 months from two wells, one within the designed treatment zone and a second significantly outside the designed treatment zone.

Table 1. Representative Chlorinated Solvent Concentrations in Representative Monitoring Wells.

Well	Post Injection (Months)	PCE (µg/L)	TCE (µg/L)	cis-DCE (µg/L)	Vinyl Chloride (µg/L)
MW-15	Baseline	327.0	213.0	498.0	2.7
In Zone	1	163.0	47.3	1020.0	9.8
	2	10.9	2.8	190.0	73.2
	9	<2	<2	<2	<2
MW-6	Baseline	13.2	26.3	102.0	30.4
Outside	1	<5	14.9	76.5	188.0
Zone	2	1.5	5.7	27.9	81.9
	9	2.7	7.8	37.9	37.5

CONCLUSIONS

The initial goal of the pilot test to demonstrate the effectiveness of introducing a stable microemulsion-based carbon substrate into the system to enhance reductive dechlorination within a specific treatment zone was successful as evident by the reduction in the mass of chlorinated ethenes to or near cleanup level concentrations, the change in the profile of chlrorinated ethene parent materials as compared with daughter products and the changes in the geochemistry of the site. The secondary goal of determining the horizontal and vertical extent of the influence of the application was demonstrated by the changes in geochemistry and total contaminant mass and profile in outlying areas.

REFERENCES

Stroo, H., Ward, C.H., (Eds.) (2010) *In Situ Remediation of Chlorinated Solvent Plumes*. U.S. Department of Defense Strategic Environmental Research & Development Program and U.S. Department of Defense Environmental Security Technology Certification Program, Springer Science+Business Media. pp. 44-48, 119-125, 366-368, 373-375.

Henry, B., Parsons, (2010) *Final Report, Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation, ESTCP Project ER-0627.* U.S. Department of Defense Environmental Security Technology Certification Program. pp. B-1 – B-3.

Weidemeier, T., Newel, C., Rifai, H., Wilson, J. (1999) *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, Inc., pp. 130-142, 175-183, 243-263.

Fetter, C., (1993) *Contaminant Hydrogeology Second Edition,* Prentis-Hall Inc., pp. 50-58, 208-213.

Henry, B., Miller, R., Hicks, J., (2004) *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*, U.S. Air Force Center for Environmental Excellence, Brooks City-Base, Texas, Naval Facilities Engineering Service Center, Port Hueneme, California, U.S. Army Corps of Engineers, U.S. Department of Defense Environmental Security Technology Certification Program, pp. 6-15 – 6-22, 6-23 – 6-24, 5-13 – 5-24.

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HIGH RESOLUTION SITE CHARACTERIZATION: CHLORINATED SOLVENT CONTAMINATION IN POROUS SEDIMENTARY ROCK

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High resolution site characterization coupled with new in-situ remedial technologies have greatly improved the rate of success in meeting remedial objectives and many relatively straightforward sites have been closed. However the most complex and difficult cases remain, and among these are sites at which chlorinated solvents as dense non-aqueous phase liquids (DNAPLs) have entered fractured bedrock aquifers decades ago.

The CORE$^{\text{DFN TM}}$ approach is primarily applicable to sedimentary rock types (e.g., limestone, sandstone, shale) which have significant matrix porosity (generally 1 to 20%). The overall framework of the approach is based on 3-D high resolution characterization of the groundwater flow system and contaminant mass distribution, considering both the fracture network within which nearly all groundwater flow occurs, and the rock matrix which comprises the bulk of the contaminant storage capacity in the system as dissolved and sorbed phase. The approach involves application of a number of complementary tools and techniques, some conventional and some recently developed and/or adapted from conventional methods, to collect depth-discrete data sets focused on both the fracture network and rock matrix. As described in detail by Parker et al. (2012), these include measurements on core samples collected from continuously cored holes along with various measurements in the core holes and application of multilevel monitoring systems (MLS).

Research and investigations at sites using this approach has resulted in some changes to conventional fractured rock site conceptual models, including:

1) While groundwater flow occurs almost exclusively in secondary porosity, the vast majority of contaminant mass is present in the primary porosity as dissolved and sorbed phase;
2) Borehole flowmeters typically identify up to 4 dominant flow zones in a given hole and investigators traditionally focus on these zones, often to the exclusion of other portions of the borehole;
3) Lined hole high sensitivity temperature logging and the distribution of contaminant mass in the rock matrix indicate that other flow zones are present, and very often most of the contaminant mass in or near source areas is associated with diffusion into the matrix off these lower yield fractures;
4) The presence of these additional fractures and more interconnectedness between fractures results in a conceptual model in which significant hydrodynamic dispersion occurs, and this coupled with matrix diffusion and sorption in the matrix results in very significant plume retardation;
5) Even with remediation of source zones, the downgradient dissolved plume does not recede because of back diffusion of contaminants from the matrix into the fractures (e.g. Parker et al., 2010);
6) Relatively small rates of degradation (biotic or abiotic) in the matrix (or on fracture surfaces) can serve to offset back diffusion to some extent.

In fractured sedimentary rock, or rock with primary porosity of greater than 1%, DNAPLs released decades ago entered rock fractures and joints and migrated downward from the point of entry to achieve a relatively stable extent. Over the next several decades the DNAPL mass originally present in fractures has dissolved away and diffused into the rock matrix adjacent to the fractures, such that at present time most or all of the mass originally present as DNAPL is now entirely in dissolved or sorbed phase in the rock matrix. This matrix diffusion results in significant retardation of the plume advance and often much of the total contaminant mass remains very close to the original source area. In many, if not most of these situations, groundwater flow occurs almost exclusively through the fractures but the vast majority of contaminant mass is present in the rock matrix. Investigations which focus exclusively on the fractures will fail to identify the location of the contaminant mass which sustains the dissolved plume. Often investigators focus on finding the most productive fractures (i.e., those transmitting water at the highest rate) and sample only those fractures or fracture zones. Experience has shown however, that in source zones the majority of the contaminant mass is often not associated with those fractures and is instead present in the matrix around lower flow rate features. In addition, because the contaminant mass is in the rock matrix and transport is controlled by diffusion, this mass will persist for decades to centuries. Most remedial technologies cannot readily address this mass. A relatively new approach to the investigation of such sites has been developed and employed successfully at many sites in North America and elsewhere. This approach, developed at the Universities of Waterloo and Guelph by Beth Parker's research group (Parker et al., 2012) is known as Characterization of Rock Environments – Discrete Fracture Network method (CORE^{DFN}). One of the key components of the CORE$^{DFN\ TM}$ approach is rock core contaminant analyses to determine the distribution of VOC mass in the subsurface. The rock core subsampling approach involves depth-discrete sampling and processing / extraction of rock core subsamples collected during drilling, with samples collected both adjacent to fractures and in the rock matrix between fractures, with the goal of understanding the extent to which contaminant mass has diffused from the fractures into the rock matrix and where this has occurred spatially.

The CORE^{DFN} approach makes use of rock cores to allow for quantification of contaminant mass, porosity, bulk density, fraction of organic carbon, diffusion rates, matrix permeability, mineralogy / geochemistry and allows for laboratory microcosm studies. The approach also takes advantage of the cored hole to conduct borehole geophysics, packer testing, and flow meter testing. Holes are lined upon completion to prevent cross connection of previously unconnected fracture zones (Sterling et. al., 2005). High sensitivity temperature logging of the lined hole is used to find more active fractures than are typically found using flow metering (e.g. Pehme et al., 2009; 2013). Once the hole has been fully investigated, the data from the core and that from the corehole are combined and used to select zones for temporal monitoring with MLS installations (e.g., Westbay, Waterloo System, Water FLUTe System described by Einarson 2006).

All of the different data types are assessed and used to modify the initial conceptual model for the site. In some cases, this may involve the use of mathematical models to get a sense of the time frames and magnitudes of back diffusion or to evaluate certain remedial options. Such modelling can employ an equivalent porous medium model at a large scale to determine head distributions, and a discrete fracture network model to assess transport in the fractures and the interaction of the fractures and the matrix (e.g. Chapman et al., 2013).

REFERENCES

Chapman, S., Parker, B.L. , Cherry, J.A., McDonald, S.D., Goldstein, K.J., Frederick, J.J., St. Germain, D.J., Cutt, D.M., and Williams, C.E. 2013. Combined MODFLOW-FRACTRAN application to assess chlorinated solvent transport and remediation in fractured sedimentary rock. Remediation Journal, 23 (3), 7-35.

Einarson, M. 2006. Multilevel Ground-water Monitoring. Chapter 11 in Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring, pp. 807-848. 2nd Ed. Edited by D.M. Nielsen. CRC Press, Boca Raton, FL.

Parker, B.L., Chapman, S.W., Cherry, J.A. 2010. Plume persistence in fractured sedimentary rock after source zone removal. Ground Water, 48(6), 799-808.

Parker, B.L., Cherry, J.A., Chapman, S.W. 2012. Discrete fracture network approach for studying contamination in fractured rock. AQUAmundi: Journal of Water Science, 60, 101-116.

Pehme, P., Parker, B.L., Cherry, J.A., Molson, J.W., and Greenhouse, P. 2013. Enhanced detection of hydraulically active fractures by temperature profiling in lined heated bedrock boreholes. Journal of Hydrology, 484, 1-15.

Pehme, P.E., Parker, B.L., Cherry, J.A., and Greenhouse, J.P., (2009). Improved resolution of ambient flow through fractured rock with temperature logs. Ground Water, 48(2), 191-205.

Sterling, S.N., B.L. Parker, J.A. Cherry, J.H. Williams, J.W. Lane Jr. and F.P. Haeni. 2005. Vertical cross contamination of trichloroethylene in a borehole in fractured sandstone. Ground Water 43(4), 557-573.

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FRACTURED ROCK BIOREMEDIATION CROSS ROADS: NEW MILLENNIUM MICROBIOLOGY VS LAST CENTURY HYDROGEOLOGY

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OVERVIEW

Our current abilities to characterize microbial communities and their capabilities to degrade compounds is far outstripping our ability to characterize with confidence the hydrogeological environments, notably bedrock, within which they operate. Scale is important – we require very little native material or groundwater to characterize the microbial community, whereas, fractured flow environments require testing at a larger scale, and at these scales the microbial community diversity, density and capabilities can widely vary. Can these differences in understanding and scale be reconciled to actually design an effective enhanced or natural attenuation bioremediation remedy?

Our ability to both identify microorganisms and their capabilities using molecular techniques is growing exponentially with concurrent decreases in cost. Over the past decade, we have moved from using high cost, low throughout molecular cloning combined with Sanger sequencing at relatively high cost to next generation sequencing (NGS) platforms. As a result, sequencing of a megabase of DNA (1 million base pairs) now costs less than 10 cents, down from $1,000 in 2003 (http://www.genome.gov/sequencingcosts). While costs for non-sequencing activities (e.g., DNA extraction) have a dropped less dramatically overall costs for microbial characterization have dropped significantly. Using NGS It is now cost effective to obtain detailed taxonomic profiles of microbial communities in environmental samples and it is increasingly feasible to sequence all the genes in a mixed microbial community (the metagenome). The seemingly inevitable endpoint is routine sequencing of the many millions of base pairs of DNA in microbial communities and the use of bioinformatics to extract the desired information including community structure, functional gene composition and possibly gene expression profiles using RNA sequencing approaches (RNA-Seq).

NGS can be used to provide high resolution characterization of microbial communities and their metabolic capability and activity, but also to uncover the existence of unknown organisms and genes. The power of NGS and its low cost combined with the very small amount of soil or groundwater required to obtain DNA for analysis, makes it cost-effective to sample environments at high densities. In contrast, our ability to characterize a fractured flow environment is advancing slowly, and is fairly similar to what it was ten to twenty years ago. Recent advances in micro-seismic measurements, distributed temperature sensing, and the development of fractured rock specific flux meters allow for more effective parameterisation at process-specific scales, however compared to the measurement scale of molecular testing, characterizing fracture flow networks are virtually infinite!

How can these measurement scales be brought into alignment? Can they? What can we learn if we can?

Attached microbial communities dominate the subsurface both in numbers and activity compared to their planktonic (free floating) brethren. In metamorphic fractured rock environments, the microorganisms will be distributed along fractures, relatively far apart, or they will form biofilms that can reduce or block the fracture aperture. In sedimentary rock, the microorganisms can exist within the secondary porosity environments where the diffusive flux of chemicals and nutrients can sustain their activity.

Regardless of the environment in which they live, the microbial biomass is relatively stationary compared to the geochemical parameters that are often used to measure microbial activity (e.g., methanogenesis, cations and anions, dissolved oxygen and pH). As a result, directly measuring microbial community structure, metabolic capability and activity

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using NGS methods could indicate where the microbial processes are occurring, and in turn inform us about the fractured flow network. In effect the microbial community would be used as biomonitors or biosensors of geochemical or other conditions. For example, if two samples have similar community structure and function, they are likely being exposed to the same geochemical conditions. If they are similar/different, or respond /similarly /differently overtime, these patterns could be used to diagnose the geochemical environment they are being exposed to and if that coincides with assumed flow paths.

Work by Smith et al. (2015) showed how the statistical analysis of 16S rRNA sequences can be used to distinguish contaminated vs uncontaminated sites, and even “encode a memory of prior contamination, even aft the contaminants have been fully degraded”.

Figure 2 shows the changes in microbial composition in a monitoring well relative to the geochemical parameters. In this case, tetrachloroethene (PCE) and trichloroethene (TCE) are relatively constant overtime, even though there was an increase in methane, suggesting a suitable anaerobic environment for dechorination. However, the taxonomic analysis shows that methanotrophs (methane consuming) population had increased. At this site, electron donor had been added upgradient of this well, and the microbial biosensors showed that the methane was likely being consumed and not produced at this location. This is consistent with the lack of PCE/TCE dechlorination pattern that would have been expected. This data indicates that the high resolution and sensitivity of NGS can be used to detect changes in the environment even where standard testing lacks the sensitivity or resolution.

In conclusion, NGS has the potential to help us understand groundwater flow regimes in fractured rock and other systems which could aid in designing effective remediation remedies.

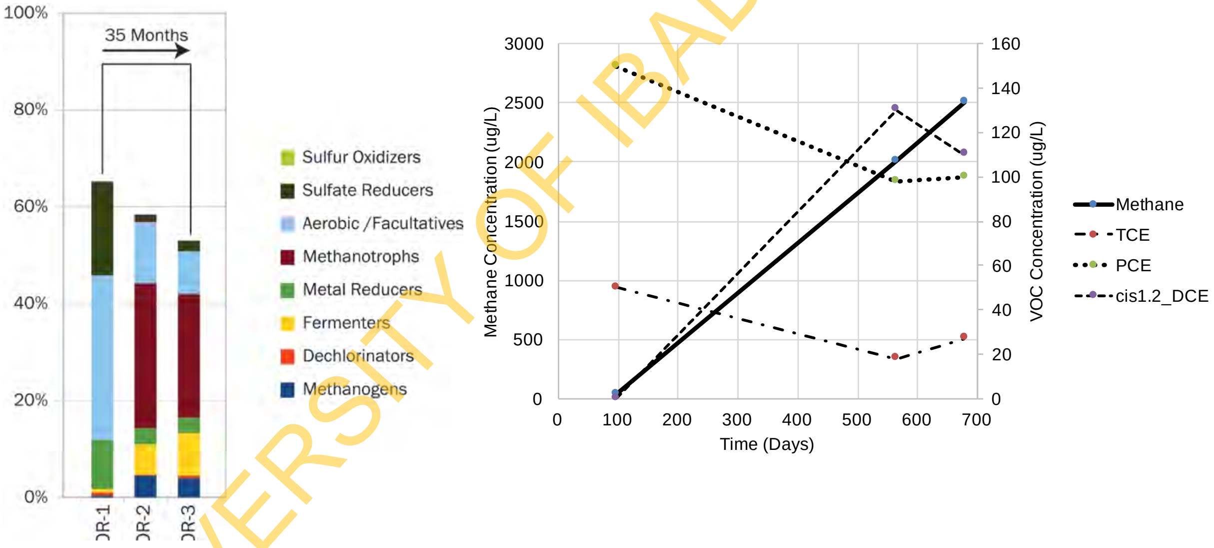

Figure 2: Comparison of microbial population composition to geochemistry

REFERENCES

Eighmy, T.T., Spear, J.C.M., Case, J., Mills, M., Newman, K., Kinner, N.E., Marbet, H., Cacas, J., Bothner, W., Coulburn, J., Tisa, L.S., Majko, M., Sullivan, E.R., and Gonsoulin, M.E. (2007) Microfracture surface geochemistry and adherent microbial population metabolism in TCE-contaminated competent bedrock. Geomicrobiol J. 24:307-330. doi:10.1080/01490450701456610

Smith, M.B., Rocha, A.M., Smillie, C.S., Olesen, S.W., Paradis, C., Wu, L., Campbell, J.H., Fortney, J.L., Mehlhorn, T.L., Lowe, K.A., Earles, J.E., Phillips, J., Techtmann, S.M., Joyner, D.C., Elias, D.A., Bailey, K.L., Hurt, Jr. R.A., Preheim, S.P., Sanders, M.C., Yang, J., Mueller, MA., Brooks, S., Watson, D.B., Zhang, P., He, Z., Dubinsky E.A., Adams, P.D., Arkin, A.P., Fields, M.W., Zhou, J., Alm, E.J., Hazen, T.C. (2015) Natural bacterial communities cerve as quantitative geochemical biosensors. mBio 6(3):e00326-15. doi:10.1128/mBio.00326-15.

THE EVOLUTION OF REMEDIATION STRATEGY FROM AN INTERNATIONAL POINT OF VIEW

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INTRODUCTION

During the early days of soil remediation, the main soil remediation objective was full removal of contaminated soil. Since then there has been a huge evolution in the business, and soil policies all over the globe have seen big changes. Depending upon the economic climate and political setting the changes varied, but in general the following phases of evolution are identified: Increasing Awareness – Full Removal – Risk Based Land Management – Sustainable Remediation (SURF-US/NICOLE/Common Forum), and there are a few countries that have proceeded further. In the Netherlands for instance sustainable subsurface use is a concept that goes further than remediation. Within this broad evolution, policies, strategies and decision making can differ. Decision making at a local level can differ significantly from developments at a national level. In the presentation the evolution is illustrated with an overview of decision tools and innovative solutions that are adopted.

RISK INFORMED AND SUSTAINABLE REMEDIATION

In the CLARINET report of 2002 European Policy Makers drafted the framework of Risk Informed Remediation. Since then, many countries are moving towards “Sustainable Remediation” in their search for cost-effective and sustainable approaches. As a direct outcome of the wider scope, it was clear that a balanced, evidence-based and transparent decision-making process was necessary, a process taking into account environmental, social and economic benefits and burdens. It was soon understood that stakeholder involvement is crucial to allow stakeholders to provide their perspectives and to communicate the unavoidable dilemmas involved. Around the globe many Sustainable Remediation Forums (SuRFs) are working on this. “Sustainability is an important general decision framework “. The first part of this paper focusses on a short global overview.

Considering the developments in remediation decision making it is possible to distinguish two main elements: 1. the evolution of appraisal or decision tools, and 2. New remediation techniques and strategies, solutions for contaminated sites.

FRAMEWORKS AND TOOLS

Many methodologies for assessing or appraising approaches for contaminated sites exist. Often already within a country more than one guideline or framework is used. Besides sustainability tools, CO_2 calculators and multi-criteria analyses, process descriptions like the NICOLE Road Map are available. A short overview of commonly known tools for sustainability appraisal will be given. Given our background we will focus on the Netherlands. Recently a tool was developed for comparing approaches for large scale contaminated groundwater (called DOG). This tool also seeks to balance benefits and impacts, and incorporates the definition of added subsurface use (suitable for drinking water extraction, heat-cold storage etc.). Like other tools it strives to make indicators measurable and comparable. We present the methodology and illustrate its added value with the application at a large area in the centre of the Netherlands.

INNOVATIVE TECHNIQUES AND STRATEGIES

The Netherlands has a long history, is densely populated and has an impressive industrial heritage. Many neighbouring countries are alike, but the level of knowledge on the scale and number of contaminated sites is unique. We know that we need innovative solutions to make our remediation program feasible from a technical and financial viewpoint. On top of this there are areas where there are many contaminant plumes that can't be dealt with separately. Reaching an agreement with all stakeholders (site owners, municipalities, water boards etc.) is a challenge. Two developments are worthwhile mentioning:

1. Strategies for area wide groundwater management; and
2. The combination with groundwater energy.

Green remediation techniques with PV cells or windmills also slowly gaining territory. But we also realize that insitu techniques (on average) will not be able to manage more than a reduction of two orders of magnitude (average concentration). Therefore, from a technology point of view, the greatest challenge lies in the agreement about reasonable and flexible remediation targets

END POINT STRATEGIES AND TOTAL COST OF OWNERSHIP

Every remediation project should come to an end. The amount of aftercare must be minimized and also come to end within a reasonable timeframe. The risk that additional remediation is required at some time in the future must also be minimized. This aspect must be an integral part of a remedial strategy. We will illustrated this with a site in Amersfoort, where renegotiation of the clean-up strategy led to the replacement of an air sparging curtain with a physical, vertical narrowing of a funnel, sufficient enough to make natural attenuation downstream, capable of dealing with the resulting flux.

The total cost of a contaminated site depends upon more than just the remediation cost. It also includes preparation and investigation costs, and of course aftercare costs. A Belgian study will be highlighted that clearly showed that increasing the budget for investigation can (and will) lead to lower remediation cost and lower total cost.

DETERMINING THE MOST APPROPRIATE REMEDIATION STRATEGY FOR A CONTAMINATED SITE

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INTRODUCTION

Determining the most appropriate remediation strategy for a contaminated site is often the single most important issue that a site owner or regulator has to resolve. Regulatory agencies have particular objectives; these are generally framed in terms of reducing the concentration of contaminants to below certain threshold values, and in some jurisdictions the practicability of achieving this outcome is taken into account. There is also increasing consideration being given to the principles of sustainability, with the objective not only being fixed on protection of human health and the environment, but also considering the benefits and trade-offs with respect to environmental, social and economic factors.

Formulation of a National Remediation Framework is underway in Australia to guide the industry on how to determine the most appropriate remediation strategy. This work is being led by CRC CARE. Formulating a Remediation Framework has prompted thinking about the decision process that should apply.

The author is involved in this work and is contributing to the preparation of various modules that will make up the Framework, and is working closely with various organisations including government, industry, the Australasian Land and Groundwater Association, SuRF ANZ, and CRC CARE. This paper presents a personal view on the issues that arise in developing guidance on determining the most appropriate remediation strategy, reflecting various of the views that are being canvassed. A structured approach to the problem is suggested, taking into account regulatory requirements and necessary endpoints, the risk perception of the various stakeholders, the town planning interface and development options, the concepts of risk-based land management, the role of institutional controls, how to facilitate development when multiple sites are involved, the role of independent review and certification, when and how to take into account the principles of sustainable remediation, and how to achieve closure and an end to the remediation process.

The approach outlined seeks to protect key environmental values, encourage a wise use of resources commensurate with the problem, consider the views of stakeholders, have a measure of what constitutes “serious” contamination and requires careful management, and how to facilitate the development of brownfields comprising many individual contaminated sites.

In summary, the sequence of considerations is as follows:

1. **Define a preliminary set of objectives**
2. **Establish consultation approach.** Identify stakeholders and consider how consultation will be carried out; develop preliminary consultation plan. Draw on well-established methods for stakeholder consultation.
3. **Assess the objectives to determine which are really essential** (eg protect human health/environment) and require strict compliance, and those which are “nice to have”. These will include key criteria relating to contamination that will protect human health and aquatic ecosystems, and also physical conditions (such as geotechnical).
4. **Identify a range of options for achieving the objectives.** This will include standard methods of remediation and development, and also more innovative methods.

5. **Consider Risk:** Determine and consider how important stakeholders perceive risk and whether they are likely to accept the outcome. Note that in this context risk will include considerations relating to the uncertainty regarding the application of technologies and containment systems, and both short term and long term management and control strategies, and the risk of failure (eg failure of remedial methods or systems, or failure of a long term containment system with release of contaminants).

   At this point, aspects of the project will be better understood, and it will be appropriate to revisit the objectives and confirm that they are appropriate and sufficient.

6. **Consider in more detail the technical feasibility, likely effectiveness, practicability and order of cost** of remedial strategies (including combinations of options) to select a set of options that will really satisfy the essential objectives. Revisit Objectives.
7. **Consider Sustainability:** consider all of the objectives and risks and environmental, social and economic (including cost) indicators - balance benefits and tradeoffs to determine which strategy(ies) are preferred (eg the set of indicators in the UK Framework can be a starting point). Involve stakeholders. Maybe use multi-criteria analysis or staged approach. Revisit Objectives.
8. **Undertake more detailed assessment of remedial strategies** that remain – resolve uncertainties. Repeat steps 5 and 6 if necessary. Obtain additional information through site investigation/trials if necessary. Involve stakeholders. Determine preferred strategy.
9. **Develop detailed Remediation Action Plan** for preferred remedial strategy, including management and control plans as may be required.
10. **Implement Plan.**

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REMEDIATION DECISION MAKING AND THE IMPORTANCE OF PROBLEM DEFINITION

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INTRODUCTION

Good remediation decision making assumes that we know enough about the environmental problem to select the optimum solution and in sufficient detail to design the solution within acceptable limits of uncertainty. However as remediation contractors our experience is that we are too often presented with remediation tenders, or requests for budget estimates, where the remediation problem is poorly defined, the remediation solution may be poorly thought through, and the associated levels of technical, regulatory and / or commercial risk around the design are unacceptable.

This presentation will discuss common problems encountered with environmental investigation and interpretation, how to avoid or mitigate them when it comes to remediation problem definition. It will focus on how to get the most out of the assessment data when defining ex-situ remediation problems and additional remediation information requirements, to reduce uncertainty and minimise technical risks when implementing a solution..

METHODS

A number of remediation case studies including both problematic and successful remediation projects, have been analysed to identify the critical factors that have resulted in technical, regulatory and commercial success and failure. The projects include the Mortlake, Newstead and Platypus gasworks, and the Lednez and Allied Feeds dioxin remediation projects.

The factors analysed included the investigation data, remediation data, clean-up standards, volume estimates, material classification and commercial delivery mechanisms..

RESULTS AND DISCUSSION

The results of the above analysis showed that many problem projects resulted from poor quantity estimates and / or poor material classification. The root cause for the above was typically inadequate definition during the investigation phase, which does not necessary result in poor remediation decision making, but typically results in failure to define and appreciate technical and associated commercial and regulatory risks, to build in the required flexibility to manage problems that may arise and a mismatch in allocating project risks through the delivery model chosen.

Successful projects resulted when the investigation and remediation data density was adequate to define remediation quantity and classification, such that technical, regulatory and commercial risk could be adequately quantified and managed, or when the commercial delivery model allocated risks to those able to manage them, and provided the flexibility to allow them to be managed.

The Mortlake gasworks remediation was an onsite encapsulation solution, undertaken on a schedule of rates basis, with stringent soil clean up criteria. Contamination of rock by tar in fractures resulted in predicted rock excavation volumes growing from 10,000 m^3 to >300,000 m^3. An example of poor quantity estimation due to inadequate investigation.

The Newstead gasworks remediation was an offsite landfill disposal solution, undertaken on a lump sum basis, with stringent soil and groundwater clean up criteria. Contamination of fill was more widespread than predicted and the deep aquifer was impacted due to a tar well placed in an erosional "hole" in the postulated base seal to the site. Predicted disposal quantities increased by 50%. An example of poor quantity estimation, due to inadequate investigation and geological understanding.

The Platypus gasworks remediation was an onsite ex-situ immobilisation solution, undertaken on a schedule of rates basis, with site specific risk based soil clean up criteria. The volume of fill was 50% less than anticipated because several investigation locations were in man-made lows (pits). The volume of contaminated rock was overestimated probably due to sampling error (contaminated fill falling into holes). Although the investigation was adequate, the geological interpretation in hindsight was not, but the overall remediation volume was less than predicted and as a consequence the financial outcome was better than predicted.

The Allied Feeds dioxin remediation was an onsite ex-situ treatment and reuse solution, undertaken on a lump sum basis, with conservative soil clean up criteria. The volume of contaminated fill significantly more than predicted due to the widespread presence of low levels of dioxin contamination. An example of poor quantity estimation, due to inadequate investigation density, with no ability to manage the risk under the commercial model used.

The Lednez dioxin remediation was essentially an onsite ex-situ treatment and reuse solution, undertaken on a lump sum basis, with site specific risk based soil clean up criteria. The volume of contaminated fill increased due to the widespread presence of low levels of "minor" contaminants. Developing further site specific risk based criteria for these compounds during the project allowed the volume risk to be managed within the project budget.

CONCLUSIONS

The main cause of problem remediation projects is unrecognised inadequate investigation and remediation data, which results in poor quantity and classification estimates, and poor remediation decision making in combination with a commercial delivery model that does not provide the flexibility to manage the problems that will inevitably arise.

Successful remediation projects are characterised by adequate investigation and remediation data, such that robust volume and classification estimates can be made, risks can be quantified and appropriately allocated, and appropriate remediation decisions be made in conjunction with a delivery model that allows the flexibility for the appropriate party to manage the risks under their control.

REMEDIATION DECISION MAKING AND MANAGING RISK AND UNCERTAINTY

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INTRODUCTION

An important adjunct to remediation decision making is effective project delivery considering the unique uncertainties and risk involved. Remediation projects are inherently risky because they typically involve many technical unknowns and may be complex in nature. As a consequence risk also applies to commercial and regulatory aspects of remediation projects. Managing technical uncertainty and the range of project risks is an important consideration in determining a projects success, and should be part of the decision making process.

Adequate problem definition prior to a project being tendered, matching the project delivery mechanism to the level of project risk and including risk management mechanisms in the remediation contract are key to achieving a successful project outcome for all the parties.

Problem definition and mechanisms like risk based standards should fall under the control of the contractor.

PROBLEM

Many projects go through years of detailed investigation aimed at determining whether there is a problem that requires positive action and determining clean-up standards and method selection but without adequate remediation data (as opposed to investigation data) before a remediation contractor is involved. This commonly results in significant time and cost over-runs to achieve project completion.

TEAM

As with other projects, having a team approach (client, consultant, project manager and EPA accredited Auditor) to a remediation project is more likely to ensure a successful outcome. However, getting the contractor into the team early can be problematic due to probity requirements, or other contractual issues.

TIME

Depending on the scale and complexity of the project, the planning and regulatory approval process may start several years before the actual works are undertaken and in several instances the final proposed solution may require a change of approval which can add significantly to the time, cost, and uncertainty of the project.

RISK MANAGEMENT

Key issues to be addressed during the planning and delivery phases of a remediation project which can reduce the uncertainty risk are:

- Ensuring that all stakeholders understand the steps required to get to remediation. Be clear with the client that a RAP is not a remediation design and ensure that the client understands the full process - not just a simplified version.
- Defining the required outcome of the remediation process – be clear on the ultimate end use and work back. Ensure that architects, planners and other key stakeholders are 'in the tent' and everyone is clear on what the process is.
- Defining the problem and solution through the development of a basis of design. This details the design and delivery of the remediation. This is not a simplified RAP, or

even a detailed RAP, but a detailed design document that specifies all the engineering inputs required for a project.

- Understanding that it will be much more difficult and costly to change course later in the process. Rather than viewing the remediation as a separate exercise, integrating the remedial works into the development outcome can add substantial value to a project.

The authors have been involved with a number of different commercial models for a variety of projects and will talk through Australian examples of remediation projects and the types of contractual models used. They will focus on risk mitigation strategies employed whilst delivering the projects, in particular:

- a contractors approach to site remediation characterisation;
- obtaining acceptable environmental conditions for the remediation;
- obtaining acceptable finance for the project;
- obtaining acceptable conditions for the subsequent development; and
- removal of regulatory notices on the sites.

REMEDIATION OF COMPLEX CONTAMINATED GROUNDWATER SITES: PERSPECTIVES ON EFFECTIVE DECISION MAKING TO MEET PROJECT OBJECTIVES

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INTRODUCTION

Extensive and costly efforts for more than 40 years have demonstrated that restoration of groundwater contaminated by releases of anthropogenic chemicals to a condition allowing for site reclassification to one of unlimited use and unrestricted exposure (i.e. "restoration") is a significant challenge and the challenge increases significantly as the complexity of the site (geology, hydrogeology, contaminant, stakeholder interests) increases. There is general agreement among practicing remediation professionals that there is a substantial population of sites, where, due to inherent geologic complexities, restoration within the next 50 to 100 years (i.e. a "reasonable time frame") is likely not achievable (NRC, 2012). Recent publications, however, present a framework for the implementation of alternative strategies for groundwater restoration at sites where clean up goals are likely not attainable, which include establishment of alternative project objectives as opposed to restoration. This could include such strategies as revision of clean up targets and/or location of points of compliance, while maintaining protection of human health and the environment through appropriate institutional controls and engineered containment systems.

METHODS

A recent study completed under the auspices of the National Research Council (NRC) (NRC, 2012) outlined a number of key findings regarding the future disposition of legacy hazardous waste sites with contaminated groundwater:

a) At least 126,000 sites across the U.S. have residual contamination at levels preventing site closure, and this number is likely an underestimate. About 10 percent of the 126,000 sites are estimated to be complex from a hydrogeological and contaminant perspective. No information is available on the total number of sites with contamination in place above levels allowing for unlimited use and unrestricted exposure, although the total is certainly greater than 126,000.
b) The estimated "cost to complete" for sites that have not reached closure is \$110-127 billion. This number is highly uncertain and likely to be an underestimate of future liabilities.
c) For the suite of currently available remedial technologies, significant limitations persist that make widespread achievement of drinking water standards unlikely at most complex contaminated groundwater sites in 50–100 years.
d) There are limited data with which to compare remedial technology performance.
e) As the understanding of chemical toxicity and dose-response relationships evolves, there could be changes in drinking water and indoor air standards for important contaminants, such as the solvent TCE. Such changes could potentially lead to determinations that existing remedies at some hazardous waste sites are no longer protective of human health and the environment.

f) Consideration of the vapor intrusion pathway is needed at all sites where volatile organic chemicals (VOCs) are present in the soil or groundwater aquifer. As a precaution, vapor mitigation may need to be built into all new construction on or near known VOC groundwater plumes.

g) At many complex sites where the effectiveness of site remediation has reached a point of diminishing returns prior to reaching cleanup goals, the transition to passive management (like monitored natural attenuation or MNA) should be considered using a formal evaluation called a Transition Assessment.

h) Cost savings are anticipated from implementation of the Transition Assessment *but funding will still be needed to maintain long-term management at these complex sites.*

i) New research is needed in many areas to support the shift to long-term management of complex sites, including remediation technology development, tools to better assess vapor intrusion and MNA, and modeling that can incorporate back-diffusion and desorption.

RESULTS AND DISCUSSION

Remedial action objectives at sites, particularly large sites with significant historical releases of hazardous chemicals into a subsurface environment with a high degree of complexity, may include some components of management (as opposed to restoration) as well as more traditional restoration objectives. Management options may include partial treatment of the source areas to reduce the risks of exposure from residual contamination, reliance on monitored natural attenuation, source isolation, institutional controls, or any combination of these approaches. In addition, at such sites, it may be appropriate to utilize alternate concentration limits, CUTEP approaches, or other alternative remedial endpoints. This presentation will attempt to translate recent US-based experiences to explore various decision-making approaches to the evaluation of remedy selection, design, and performance based on site-specific complex characteristics of particular interest in the Australian environment.

CONCLUSIONS

The focus of effective decision making needs to be on strategies that can transition such sites into a long term management plan that will reduce life cycle costs while maintaining desired human health and environmental protection goals and minimizing risks of unintended exposure to residual contamination. Ultimately, this transition process should result in resource-respectful, timely, and cost-effective remedial decisions that comply with existing environmental regulations, are protective of human health and the environment over the long term, and avoid costly expenditures with minimum impacts on risk reduction.

REFERENCES

National Research Council. (2012) Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites, Water Science and Technology Board, NAS Press, Washington, DC

PERMEATION PASSIVE SAMPLING IN ENVIRONMENTAL ANALYSIS

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INTRODUCTION

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium due to a difference in chemical potential of the analyte between the two media. It has many advantages compared to active sampling, including simplicity, low cost and no need for trained personnel. A new permeation-type passive sampler has been developed at the University of Waterloo and is available commercially under the name “Waterloo Membrane Sampler” (WMS). It uses mostly off-the-shelf components, which makes it simple and inexpensive. In WMS, a polydimethylsiloxane (PDMS) membrane separates the sampled medium from the sorbent. Analyte uptake rate is determined by the permeability of the membrane to a given analyte.

METHODS

The design of the WMS is shown in Figure 1.

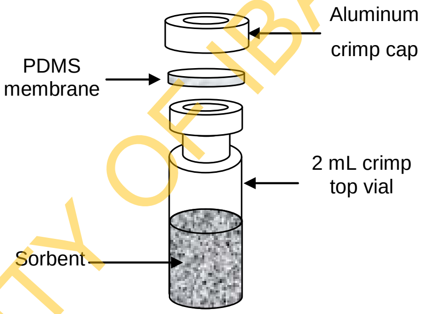

Figure 1: Waterloo Membrane Sampler design

The sampler is made of a standard chromatographic vial whose volume depends on the application. It is partly or completely filled with an appropriate adsorbent, and sealed with a custom-made PDMS membrane of strictly controlled geometry. For the exposure, the sorbent is brought to direct contact with the membrane. Analytes can be liberated from the sorbent using solvent extraction or thermal desorption

RESULTS AND DISCUSSION

The WMS has been originally developed as a kinetic passive sampler for the determination of time-weighted average concentrations of volatile organic compounds (VOCs) in air. The theory of its operation has been extensively developed and tested. Conversion of the analyte mass collected by the sorbent during exposure to the time-weighted average concentration of the analyte in air during sampling requires the knowledge of the calibration constant of the sampler for each analyte of interest, Experimental determination of these constants is tedious and labour-intensive. Owing to the mechanism of analyte transport across PDMS membranes, the calibration constants of the sampler can be estimated from the linear temperature programmed retention indices (LTPRI) of the analytes determined using GC columns coated with pure PDMS stationary phases. Apart from greatly simplifying the calibration of the samplers for target analytes, the method proposed makes it possible to

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quantify pollutants whose identity is unknown at the time of the exposure. In addition, the effect of environmental factors on the sampler performance was characterized.

Determination of VOC concentrations in soil gas presents a unique set of challenges. Starvation effect can be very significant in soil gas sampling because of the low permeability of many types of soil. A mathematical model developed to mimic soil gas sampling conditions indicated that moisture content is a significant variable contributing to the potential low bias of passive soil gas measurements collected from a typical borehole. Uptake rates of up to 1 mL/min can be used under conditions of water saturation of 40%. Based on these result, a modified version of the WMS with reduced uptake rate has been developed and tested for soil gas sampling. A comparison of the results obtained with the WMS with those obtained using SUMMA canister sampling obtained in field tests demonstrated excellent agreement as illustrated in Figure 2:

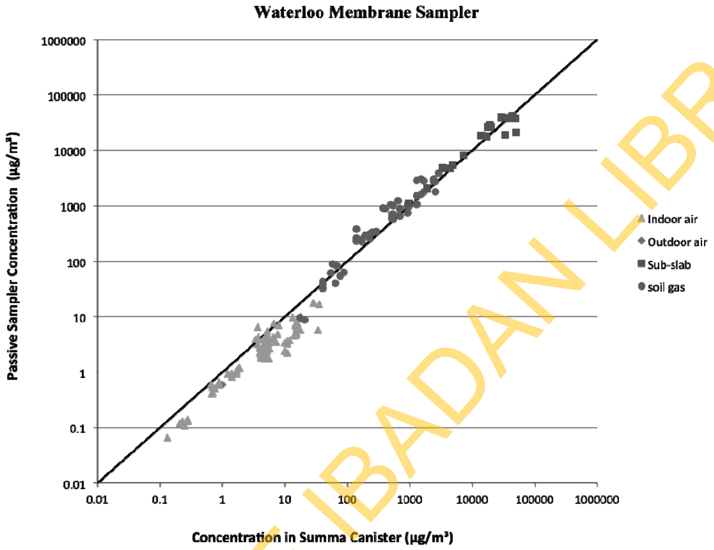

Figure 2: Correlation between WMS and Summa Canister results for field tests

With a slight modification, the sampler can be used for sampling lasting up to several months, which is of particular importance in vapor intrusion studies.

Compound specific isotope analysis (CSIA) is used extensively for fingerprinting applications and for the evaluation of the degradation processes in organic contaminant studies. The suitability of the WMS as a sample preconcentration tool for CSIA was examined. The sampler introduced small isotopic fractionation, but its extent was independent of analyte concentration, sampling time and temperature.

WMS was also tested for VOC preconcentration from water. Linear responses were observed with sub-ppb limits of detection. Finally, the sampler was tested for the extraction of VOCs from bulk soil samples. Near-quantitative extraction was possible under optimized conditions for a variety of soil types in a purely passive process requiring no sample handling.

CONCLUSIONS

Waterloo Membrane Sampler in various configurations is capable of sampling all major compartments of the environment (air, water and soil). This makes it a unique and versatile tool for environmental analysis.

ACKNOWLEDGEMENTS

The authors thank Natural Sciences and Engineering Research Council of Canada, ESTCP, ORF, MITACS, OCE, University Solvent Consortium and Geosyntec Consultants for the financial support of this research.

A NEW METHOD FOR PERIMETER SAMPLING OF VOCs – “U.S. EPA METHOD 325: VOLATILE ORGANIC COMPOUNDS FROM FUGITIVE AND AREA SOURCES”.

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INTRODUCTION

EPA Method 325, “Volatile Organic Compounds from Fugitive and Area Sources” is a new fence-line monitoring method about to be finalised by the U.S. EPA. This method will be suitable for a number of ambient air monitoring applications. It includes 2 sub-parts being EPA 325A: “Sampler Deployment and VOC Sample Collection” and companion method EPA 325B: “Sampler Preparation and Analysis”.

Diffusive sample collection techniques for measuring VOCs have been in use since the 1980’s and there are a number of International Standards describing the procedures for measuring ambient, indoor and workplace air.

The method was developed to enable refineries to comply with the updated U.S. Federal regulation CFR40 (parts 60 and 63) and is expected to become compulsory in the U.S.A in the near future (mid 2015). It will require ongoing 2 week passive (diffusive) sampling of VOCs onto sorbent tubes at a number of locations around the boundary of petroleum refineries.

In addition to perimeter monitoring at petroleum refineries, EPA Method 325 has applications in a number of air monitoring situations requiring time integrated passive environmental monitoring for periods of up to 4 weeks.

EPA Method 325 – Volatile Organic Compounds from Fugitive and Area Sources

This is the first method from the U.S. Environmental Protection Agency (EPA) describing the use of passive samplers for measuring environmental levels of VOCs for risk assessment. This method describes collection of VOCs at a property boundary or from fugitive and area emission sources using passive (diffusion) samplers. The EPA produced the method following a number of studies including a year-long field study investigating and validating the performance of this type of monitoring.

It is a robust method providing reliable data with little effect from changes in ambient weather conditions. There are many benefits when applied to ambient or perimeter sampling. These include low detection limits, high accuracy and precision, results are time integrated over a number of days, pumps are not required to collect the samples and the method is easy to use in the field as well as being relatively low cost.

EPA Method 325A - “Sampler Deployment and VOC Sample Collection”

This part of the method describes the deployment of unobtrusive passive sampling tubes around the perimeter of the site. They are typically left for extended periods (e.g. 14 days) to monitor criteria pollutants such as benzene. The method requires multiple samples per site as well as the collection of duplicate samples and inclusion of trip blanks.

The size and shape of the area to be monitored will determine how many samplers will be required and where they will be placed.

EPA Method 325B - "Sampler Preparation and Analysis"

This method describes the procedures for preparation of sampling tubes and shipment and storage of the exposed sampling tubes. It also covers laboratory analysis of the samplers and quality control procedures such as analysis of trip blanks and method blanks. The samples are analysed using TD-GC/MS (Thermal Desorption Gas Chromatography Mass Spectrometry).

The diffusive passive sampler collects VOCs from air for a measured time period at a rate that is proportional to the concentration of vapour in the air at that location.

As an example, the detection limit for Benzene in air has been shown in Table 1 to demonstrate the sensitivity of the method over various exposure times.

Table 1. Detection limits for benzene in air for various exposure periods.

Exposure Period *(days)*	7	14	21
Benzene Level *(µg/m³)*	0.8	0.4	0.2

The sampling methodology can be used to measure many compounds in addition to benzene including butadiene, toluene, ethylbenzene, xylenes and a range of other hazardous air pollutants.

CONCLUSIONS

This new USEPA Method 325 is a robust method providing reliable data with little effect from changes in ambient weather conditions. There are many benefits when applied to ambient or perimeter sampling. These include low detection limits, high accuracy and precision, results are time integrated over a number of days, pumps are not required to collect the samples and the method is easy to use in the field as well as being relatively low cost.

The method will have numerous applications on sites where time integrated air sampling is required for risk assessment.

REFERENCES

EPA Method 325, Volatile Organic Compounds From Fugitive and Area Sources, US Federal Register, 40 CFR Parts 60 and 63, Vol. 79, No. 125, 30 June 2014, Proposed Rule, Appendix A to Part 63 – [Amended], pages 37046 – 37075.

EN14662-4: Ambient air quality – standard method for the measurement of benzene concentrations. Part 4: Diffusive Sampling followed by thermal desorption and gas chromatography.

ISO 16017 - 2: Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling

EN14662-4: Ambient air quality – standard method for the measurement of benzene concentrations. Part 4: Diffusive Sampling followed by thermal desorption and gas chromatography.

ASTM D6196 -03 (2009): Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis for Volatile Organic compounds in Air.

US EPA Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air using Active Sampling Onto Sorbent Tubes.

RAPID ASSESSMENT OF A LARGE INDUSTRIAL MANUFACTURING SITE USING WMS-LU PASSIVE SOIL VAPOUR SAMPLERS

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INTRODUCTION

Edge Group Pty Ltd (Edge) was engaged to complete a preliminary assessment (PA) of a large active industrial facility (the Site). The purpose of the work was to investigate potential soil and/or groundwater sources of chlorinated solvent impacts previously identified in groundwater at the Site (inferred to be likely sourced from the Site).

Key contaminants of concern (CoC) selected for assessment at the Site included: tetrachloroethene (PCE); trichloroethene (TCE); dichloroethene (DCE, specifically cis-1,2-DCE); vinyl chloride (VC); volatile total recoverable hydrocarbons (TRH C_6-C_{10}); and benzene, toluene, ethylbenzene, xylenes and naphthalene (BTEXN).

METHODS

In order to perform a robust PA of multiple operational areas across the Site, while minimising disruption to ongoing Site operations, a passive soil vapour (PSV) sampling program was performed.

Waterloo Membrane Sampler – Low Uptake (WMS-LU) samplers were selected to complete the PSV assessment given:

- WMS-LU sampler uptake rates were suited to Site conditions (minimising potential soil vapour (SV) starvation effects in the low permeability basaltic clay near surface geology);
- WMS-LU samplers could be analysed in Australia, using National Association of Testing Authorities (NATA) accredited methods;
- WMS-LU analytical results can be used to calculate semi-quantitative SV contaminant concentrations allowing initial screening against published criteria.

The PSV assessment completed at the Site included the deployment of 73 WMS-LU samplers in a combined grid and targeted approach across the Site; making this one of the largest single-site deployments of WMS-LU samplers completed to date in Australia.

RESULTS AND DISCUSSION

The SV and soil sample analytical results indicated a predominating groundwater source, as limited soil impacts were noted. **Table 1** summarises the results of the PSV assessment, showing the range of recorded SV screening criteria[1] exceedances at the Site.

Table 1. SV screening criteria exceedances – concentration ranges

Analyte	Units	Screening Criteria	Concentration Range (> criteria)
PCE	µg/m^3	8,000	16,000 – 150,000
TCE		80	110 – 180,000
DCE		300	330 – 150,000
VC		100	110 – 24,000
TRH F1 (C_6-C_{10} less BTEX)		680,000	850,000 – 11,000,000

The soil and SV results showed a strong correlation to known potential source areas, and also identified impacts in two previously unsuspected source areas (using contaminant isopleth plots generated by SiREM). The data provided an indication of the level of degradation of chlorinated solvent impacts.

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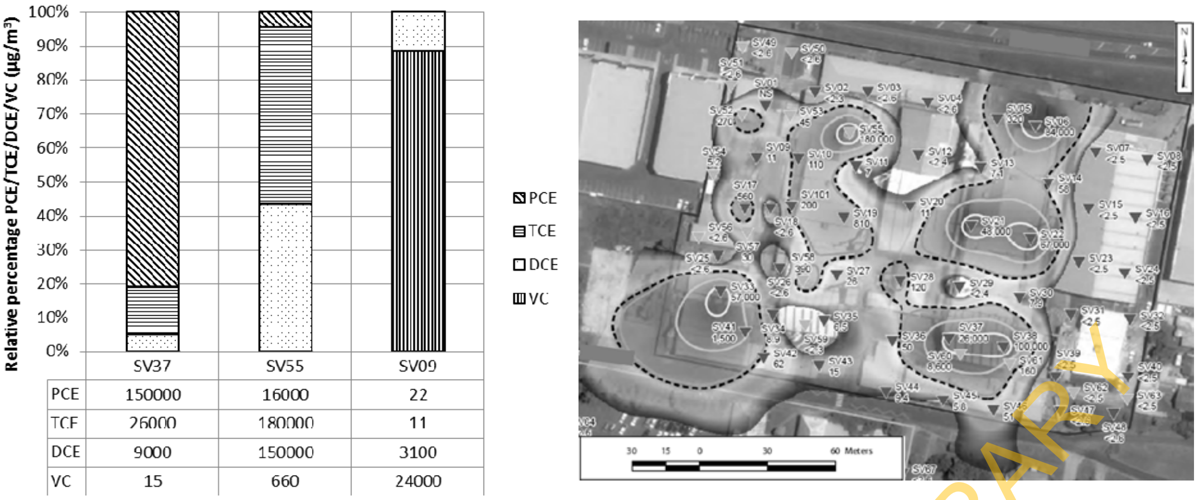

	SV37	SV55	SV09
PCE	150000	16000	22
TCE	26000	180000	11
DCE	9000	150000	3100
VC	15	660	24000

Fig. 1. Typical PCE (SV37), TCE/DCE (SV55) and VC dominant SV results, indicating variability in contaminant type/degradation; and example isopleth plot for TCE in SV across the Site (dotted line represents adopted criterion, units in µg/m^3) (after SiREM 2015)

CONCLUSIONS

The site wide PSV assessment using WMS-LU samplers achieved the following outcomes:

- identification of areas of SV impacts, with distinction between chlorinated solvent and petroleum hydrocarbon source areas, and completion of a PA of likely soil and/or groundwater source media;
- rapid site wide screening while minimising disruption to the ongoing operation of the Site;
- SV results obtained across a wide concentration range in low permeability geology (clays), without starvation effects; and
- cost saving over traditional assessment methods, while providing a greater data resolution. Further cost savings are likely through the ongoing use of data from this assessment to inform future works.

REFERENCES

CRC CARE (2013), *Petroleum hydrocarbon vapour intrusion assessment: Australian guidance*, CRC CARE Technical Report no. 23, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Davis, G.B., Wright, J. and Patterson, B.M. (2009), *Field Assessment of Vapours*, CRC CARE Technical Report no. 13, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Friebel, E. and Nadebaum, P. (2011), *Health Screening Levels for Petroleum Hydrocarbons in Soil and Groundwater*, CRC CARE Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

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[1] SV Screening Criteria Used - National Environmental Protection Council (1999 as amended 2013), *National Environmental Protection (Assessment of Site Contamination) Measure (NEPM)*, Schedule B1, Federal Register of Legislative Instruments F2013L00768, Interim Health Investigation Levels and Health Screening Levels (HSLs) for commercial/industrial land use, and US Environmental Protection Agency (2015), Regional Screening Levels (USEPA RSLs) for commercial/industrial land use.

[2] Soil Screening Criteria Used - NEPM HSLs, NEPM Ecological Screening Levels and USEPA RSLs for commercial/industrial land use.

A COMPARISON OF PASSIVE SAMPLING AND LOW-FLOW OR BAILED SAMPLING RESULTS ACROSS A RANGE OF AUSTRALIAN HYDROGEOLOGICAL SETTINGS

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INTRODUCTION

The availability of no-purge groundwater sampling technologies offers the opportunity to undertake more cost-effective and sustainable approaches to groundwater monitoring in the management of contaminated sites. A number of studies indicate that groundwater samples collected without prior purging (no-purge sampling) can produce results under specific conditions that are comparable to samples collected through conventional purging methods (Byrnes et al., 1996; Bealer et al., 1998; API, 2000; Savoie & LeBlanc, 2012). ERM working with Viva Energy Australia (Viva Energy) developed a programme of trialling and evaluating no-purge groundwater sampling on a range of sites within Viva Energy's portfolio.

METHODS

Technology Selection

The initial project step was the evaluation and selection of a range of no-purge technologies to trial. Based on review of available no-purge sampling technologies the HydraSleeve™ was selected as it was considered to suit a broader range of analytes and to be more cost effective than alternative methods.

Site Evaluation

Consistent with ITRC (2006) guidance, the study evaluated 145 sites within a portfolio of petroleum hydrocarbon sites for appropriate conditions for no-purge sampling. The portfolio includes sites across Australia and represents a range of hydrogeological conditions. Trial sites for no-purge sampling were selected where water quality within a monitoring well screen was considered most likely to be representative of groundwater in the aquifer. The conditions considered to lead to this scenario were:

a) Unconfined aquifers with monitoring wells screened across the groundwater table;
b) Unconsolidated aquifers;
c) Aquifers with moderate to high groundwater flow velocities;
d) Monitoring wells that have been well developed and are free from biofouling;
e) Sampling for petroleum hydrocarbons only; and
f) No measureable non-aqueous phase liquids (NAPL) in the monitoring well.

In addition to the site conditions outlined above, no-purge sampling trials were conducted at sites where high-precision sampling was not required and where results from sampling methods that employed purging were available for comparison. Sites near monitoring endpoints with regulators were also excluded. Across the portfolio, 77 of the 145 sites reviewed (53%) were found to be suitable for the no-purge sampling trials.

Groundwater Sampling

For sites and wells selected for no-purge sampling, Hydrasleeve™ grab samplers were deployed within the screened interval at depths based on the well's position relative to the plume source area and on observations made during the drilling and/or historical sampling of the well. This was done to best target the water column interval where hydrocarbon concentrations were expected to be highest.

For the purposes of comparing no-purge to more recognised sampling methods, at three sites sampling was completed within a week of the no-purge trial using the purge and bail or low flow techniques historically used on site. The data analysis and review in this paper focuses on the results for TRH C_6-C_{40} and BTEX from these three sites.

The three sites evaluated are: Site A with an unconsolidated sand aquifer (8 wells), Site B with a weathered shale aquifer (4 wells), and Site C with a fractured basalt aquifer (15 wells).

RESULTS AND DISCUSSION

For Site A and Site B, which were characterised by unconsolidated aquifers, the no-purge results provided reasonable results when compared to both the corresponding low-flow sampling and historical results. The relative percent difference (RPDs) of no-purge BTEX and TRH C_6-C_{10} results compared to the low flow results ranged from 10% to 130% and were consistent with the range of RPDs for site field duplicates. It is noted the higher range of RPDs were from lower concentration (less than 500 µg/L) samples. The RPDs for TRH $>C_{10}$-C_{16} ranged from 0% to 366%. Where the RPDs for TRH $>C_{10}$-C_{16} exceeded the site field duplicates range, the no-purge sample results reported higher than the low flow sample.

By contrast results from Site C, located in a fractured basalt aquifer, indicated that the connectivity of specific wells, presumable through the fracture network, and the aquifer's response to pumping were controlling factors in how results from the no-purge sampling compared to those from more traditional purging methods. At one well, results from the no-purge sampling were several orders of magnitude below previous results; at another well, results from the no-purge sampling over predicted those from low flow sampling. At this site, differences in results between the two sampling methods did not appear to be related to the analyte or to the concentration range.

CONCLUSIONS

The results show that where the criteria are consistent with those presented in ITRC (2006) guidance, no-purge sampling is likely to be a suitable technique for groundwater monitoring with suitable hydrogeological and well conditions as well as suitable site data quality objectives. In fractured rock environments, variations in fracturing and groundwater pathways may results in no-purge sampling results that are not comparable to those from purging-based sampling methods.

REFERENCES

American Petroleum Institute, 2000: No-Purge Groundwater Sampling. An Approach to Long-Term Monitoring.

Bealer, L. J., Byrnes, J. P., and Springer, K., 1998: No purging in ground-water sampling proposal for gasoline compounds in New Jersey unconfined aquifers, in, Procs, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation Conference, NGWA, Houston, Texas, Nov. 11-13, 1998, 474-482.

Byrnes, J. P., Briglia, J. E., and Bealer, L. J., 1996: Evaluation of well purging in ground-water sampling for BTEX and MTBE, in, Procs of the Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation Conference, NGWA, Houston, Texas, Nov. 13-15, 1996, 221-235.

Savoie, J.G., and LeBlanc, D.R., 2012: Comparison of no-purge and pumped sampling methods for monitoring concentrations of ordnance-related compounds in groundwater, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010: U.S.G.S.,Scientific Investigations Report 2012–5084.

ITRC 2006: Technology Overview of Passive Sampler Technologies. Prepared by the Interstate Technology & Regulatory Council (ITRC) Diffusion Sampler Team. March 2006.

PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOIC ACID (PFOA): ECOTOXICITY AND ENVIRONMENTAL CONCERNS

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INTRODUCTION

During the past 50 years, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) containing chemicals have been widely used throughout the world in fire fighting foams and a variety of industrial and house-hold products. Consequently, PFOS and PFOA have become ubiquitous in the environment and recently recognised as emerging contaminants of public concern due to their toxicity and extremely persistent nature. There is a paucity of information on the toxicity of PFOS and PFOA to soil and aquatic organisms. Hence we have investigated the negative effects of PFOS and PFOA on a range of terrestrial and aquatic organisms including gene expression in earthworm.

METHODS

Three soils (neutral and alkaline soils collected from South Australia and an OECD artificial soil) differing in their physicochemical properties were used in this study. Avoidance behaviour, mortality and differential gene expression in earthworms (*Eisenia fetida*) were studied following the standard procedures described elsewhere (Caceres et al., 2011; Mayilswami et al., 2014)). Growth inhibition of algae (*Raphidocelis subcapitata* and *Chlorella vulgaris*) and mortality in water-flea (*Daphnia carinata*) were studied according to Megharaj et al. (2000) and Caceres et al. (2007).

RESULTS AND DISCUSSION

The LC_{50} values (lethal concentration that caused 50% mortality) for earthworms greatly differed depending on the chemical and also the nature of soil. In general PFOS was more toxic than the PFOA. Interestingly the artificial soil exhibited greater toxicity than the natural soils. Thus the LC50 values for PFOS in neutral, alkaline and OECD soils were 446.8, 366.7 and 159.9 mg/kg soil, respectively. Similarly, the LC50 values for PFOA in neutral, alkaline and OECD soils were 894.9, 823.8 and 672.1 mg/kg soil, respectively.

Differential gene expression study revealed that chronic exposure of *E. fetida* to PFOS alters the expression of calcium homeostasis and neuronal development related genes. Where as, PFOA predominantly affected the genes that are involved in apoptotic process, reproduction, calcium signaling, neuronal development and lipid metabolism.

Toxicological tests revealed bioaccumulation of PFOS and PFOA in earthworms exposed to contaminated soils and inhibition of soil enzyme activities that are important for maintaining soil health. Further results of these investigations on the toxicity and persistence of PFOS and PFOA under aquatic and terrestrial environments will be discussed.

CONCLUSIONS

PFOS was found to be more toxic than PFOA to earthworms in terms of mortality. Further the OECD artificial soil exhibited higher toxicity than natural soils for both PFOS and PFOA in earthworms. Chronic exposure of earthworms to PFOS and PFOA even at 10 mg/kg soil led to an alternation in expression of genes involved in several important functions in the organism.

REFERENCES

Caceres, T., Megharaj, M. and Naidu, R. (2011).Toxicity and transformation of insecticide fenamiphos to the earthworm *Eisenia fetida*. Ecotoxicology 20: 20-28.

Mayilswami, S., Krishnan, K., Megharaj, M., Naidu, R. (2014). Chronic PFOS exposure alters the expression of neuronal development- related human homologues in *Eisenia fetida*. Ecotoxicology and Environmental Safety 110:288-297.

Megharaj, M., Singleton, I., McClure, N.C. and Naidu, R. 2000. Influence of petroleum hydrocarbon contamination on microalgae and microbial activities in a long-term contaminated soil. Archives of Environmental Contamination and Toxicology 38: 439-445.

Cáceres, T., He, W., Megharaj, M. and Naidu, R. (2007). Toxicity of chlorpyrifos and TCP alone and in combination to *Daphnia carinata*: the influence of microbial degradation in natural water. Water Research 41: 4497-4503

INNOVATIVE TECHNOLOGIES ON TREATING PERFLUOROALKYL SUBSTANCES

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INTRODUCTION

Poly- and Perfluoroalkyl substances (PFASs) make up a group of compounds that have extreme thermal and chemical stability because of the strong fluorine−carbon bond (~110 kcal/mol). Due to their unusual characteristics, PFASs have been used in nearly every aspect of daily lives. Although the excellent chemical inertness is a huge advantage in the application of PFASs, it also causes considerable environmental concerns because of their ubiquitous presence in the environment and toxicity to animals and potentially human. High concentrations of PFASs were frequently detected at sites impacted by aqueous film-forming foam (AFFF) in firefighting practices (Houtz et al, 2013). The National Health and Nutrition Examination Survey (NHANES) conducted by the Centers for Disease Control and Prevention (CDC) in 1999 revealed that perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA) were present in all the human serum samples in the United States (Calafat et al, 2007). Contaminated water treated with granular activated carbon has been the most common practice to remove PFASs, however, poor treatment of short-chain PFASs and increases in PFOA/PFOS concentrations in effluent have made this technology questionable on treating AFFF waste or ground waters. Several studies reported using electrochemical, photolytic, or sonochemical oxidation and catalyzed hydrogen peroxide propagation to break down PFASs. These approaches require large energy inputs, and special devices, thus limit their full-scale applications. For potential remediation applications, it is desirable to identify an approach that can decompose PFASs under naturally relevant conditions.

METHODS

Enzyme-catalyzed oxidative humification reactions (ECOHRs) could serve such a role but have not been well examined. ECOHRs refer to an important class of reactions that are facilitated by fungal extracellular enzymes to mediate the polymerization of small molecule humic precursors into humic substances in the environment. These enzymes oxidize phenolic or anilinic substrates into radical and quinone intermediates that are further covalently bound with each other via coupling. The active intermediates formed during ECOHRs can also attack other persistent organic compounds such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), thus incorporating them into humification and leading to their decomposition and detoxification (Fig. 1). This study investigates the possibility and mechanisms of PFASs (with use of PFOA as model PFASs) degradation by ECOHR.

RESULTS AND DISCUSSION

Approximately 50% of PFOA in a mineral buffer solution decomposed after 157 days with a pseudo-first-order rate constant of 0.0044 day−1(r2 = 0.89). No shorter carbon-chain PFCAs were detected as degradation products during the experiment. However, partially fluorinated shorter-chain alcohols and aldehydes were identified by high-resolution mass spectrometry. These partially fluorinated compounds were likely products resulting from PFOA degradation via a combination of free radical decarboxylation, rearrangement, and coupling processes. Fluoride was detected in the reaction solution, and the concentration indicated a 28.2% defluorination ratio during the treatment. This finding suggests that PFOA has been transformed during humification, and ECOHRs can potentially be used for the remediation of

PFOA. PFOA degraded significantly in both water solution and soil via laccase mediated ECOHRs.

CONCLUSIONS

This study indicates that ECOHR can effectively transform PFOA to shorter-chain, partially fluorinated products in the presence of organic mediator. Because these products are seemingly analogues of PFCA precursors, it is possible that some of them may be further transformed to their corresponding shorter-chain PFCAs under extreme oxidative conditions, but these partially fluorinated products, as well as shorter-chain PFCAs, are believed to be more environmentally benign. It should be noted that laccase substrates with phenolic functional groups are abundant in natural organic matter, which may serve as mediators for ECOHRs. Such natural processes may effect only very slow PFOA degradation given the low PFOA concentrations and variable humification enzyme activities in the natural environment, but it is possible to enhance the humification reactions through an engineering approach for remediation purposes.

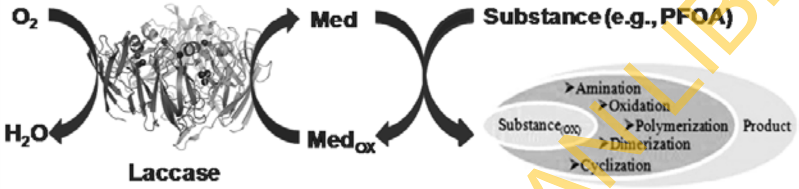

Fig. 1. ECOHR Scheme

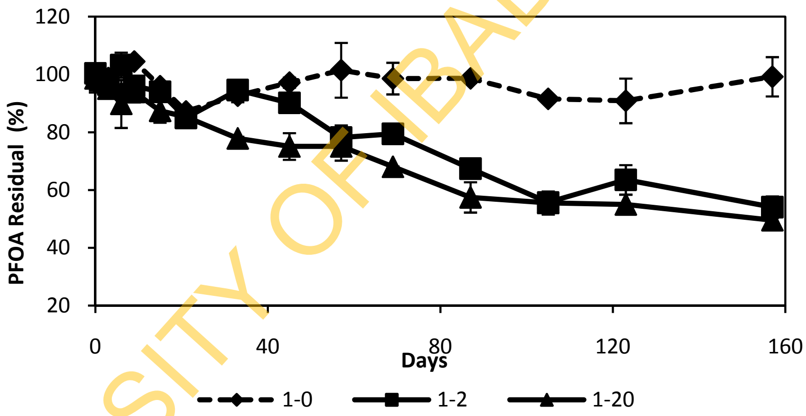

Fig 2. PFOA residual (%) changes over time in aqueous solution. 1-0: 1 U/mL PO + no HBT; 1-2: 1 U/mL PO + 2 μM HBT; 1-20: 1 U/mL PO + 20 μM HBT.

REFERENCES

Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. (2013) Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. Environ. Sci. Technol. 47, 8187−8195.

Calafat, A. M.; Kuklenyik, Z.; Reidy, J. A.; Caudill, S. P.; Tully, J. S.; Needham, L. L. Serum Concentrations of 11 Polyfluoroalkyl Compounds in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 1999−2000 (2007) Environ. Sci. Technol. 41, 2237−2242.

Qi, Luo; Lu, Junhe; Zhang, Hao; Wang, Zunyao; Feng, Mingbao; Chiang, Sheau-Yun Dora; Woodward, David and Qingguo Huang (2015) Environ. Sci. Technol. Letter **2015**, *2* (7), 198–203.

WC23

C6 SHORT-CHAIN FLUOROTELOMERS PROVIDE A BETTER ENVIRONMENTAL SOLUTION AND SUPERIOR PERFORMANCE FOR CLASS B FIREFIGHTING FOAM APPLICATIONS

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INTRODUCTION

Fluorochemicals have become stereotyped by the adverse effects of PerFluoroOctanyl Sulfonate (PFOS) from the Electrochemical Fluorination (ECF) Process –. No longer used except in China. Persistent, Bioaccumulative and Toxic (PBT), PFOS is also the only fluorochemical of around 40,000 known, currently listed as a Persistent Organic Pollutant (POP) under the Stockholm Convention, along with many pesticides.

PFOS is widely distributed in people. In 2003-4, the US National Health and Nutrition Examination Survey found average blood serum levels of PFOS in the American population of 20 parts per billion (ppb).

Tendencies to suggest “all fluorochemicals must behave like PFOS”, mis-represents safer short-chain alternatives, so this sets the record straight with factual reference-based material.

DISCUSSION

How PFOS is thought to arrive in the general population is reviewed from Environmental Working Group (2015) findings, confirming treating with stain repellents (eg.carpets and food packaging) could be significant sources, and may explain why children’s levels are higher.

The need for fluorochemicals in firefighting foams is summarised. Fast knockdown achieved from film forming characteristics and essential fuel shedding capabilities are provided by these fluorinated surfactants. Jho’s (2012) research showed without these additives, Fluorine Free Foams (F3) are vulnerable to attack and sudden unexpected flashbacks, caused by fuel mixing with detergent (hydrocarbon surfactants) in the foam bubbles. This substantially increases safety risks for casualties and emergency responders, particularly when forcefully applied. Schafer’s (2007) research showed three times more F3 is often be required on a given sized fire, compared to Aqueous Film Forming Foams (AFFF) - a consequence of fluorine being absent. Usually F3 extinguishment takes longer, allows more noxious breakdown production, greater risk of life safety and incident escalation, more property damage plus business interruption.

These special fuel shedding capabilities can be retained without the major environmental drawbacks of PFOS by using C6 short-chain fluorotelomer surfactants, which already have a proven record of saving lives and properties for the US Military and Aviation applications.

Issues of persistence and its definition are clarified to avoid some misleading assertions, as are differences in aquatic toxicity impacts of these C6 and alternative F3 agents. F3 agents are typically ten times more toxic than C6 based foams due to much higher detergent loadings. Fate and behaviour studies of C6 based foams show they are not bioaccumulative, nor biomagnifying, nor toxic, nor carcinogenic, nor mutagenic, nor reproductive nor developmental toxicants. Environ’s assessment (2014) against potential POP listing showed C6 fluorotelomers only met one (persistence) of the four essential criteria required to become POP listed. C6 breakdown products are shown to have a short average half-life in humans of 32 days compared to 5 years for PFOS, with excretion through the urinary system.

Rotander's (2015) study of Queensland firefighters showed novel fluorochemicals found in their blood were all related to PFOS and derived from the ECF process. No C6 fluorotelomer substances were found in any of these firefighters or the control group studied. Despite reduced mortality rates from a strong "healthy worker" effect, Monash University's (2014) broader Australian firefighter study found a trend of increasing prostate cancer and melanoma incidence in firefighters, with an observed increased trend from attending vehicle fires. It recognised that a wide range of hazards are encountered at fire scenes including particulates, toxic gases, Polycyclic Aromatic Hydrocarbons (PAHs), oxidation and pyrolysis products - many known to be carcinogens. 80-87% of fires attended were either structural, bush or vehicle fires which would not require Class B fluorinated foam usage. Fire and Rescue specialists confirm the use of fluorine free Class A foams is likely,but many require only water.

CONCLUSIONS

Fluorinated surfactants in foam are undesirable but necessary, particularly in large high hazard applications of volatile flammable liquids (hydrocarbons and polar solvent chemicals).C6 short-chain fluorotelomer based foams help to minimise these undesirable environmental impacts, while still achieving the reliable, fast effective and efficient fire performance we have come to expect, allowing firefighters to safely and quickly deal with these incidents, minimising the adverse environmental impacts.

The alternative, using F3 causes many problems, particularly eliminating the fuel shedding capability and increasing detergent loadings, reduced firefighter safety, typically higher application rates, and longer extinction times at fire incidents. Longer burn times produce more noxious atmospheric pollution, more run-off containing fire breakdown products with potentially a 30 times increase in toxicity to aquatic organisms from the F3. Depending on burning materials involved, this may also contain various fluorochemical breakdown products including PFOS from stain repellents and waterproofing agents. Recognising that all foams and all firewater runoff present a pollution hazard, but using the foam most effective at putting out the fire, as the UK Environment Agency (2014) suggested, would seem to be the best approach to deliver a better environmental solution and deliver greatest net benefit to society at large.

REFERENCES

CDC-NHANES (2009) Fourth National Report on Human Exposure to Environmental Chemicals http://www.cdc.gov/exposurereport/pdf/fourthreport.pdf

Environmental Working Group (2015) Poisoned Legacy: PFC Contamination: No Place to Hide http://www.ewg.org/research/poisoned-legacy/pfc-contamination-no-place-hide

Jho C (2012) Flammability and degradation of fuel contaminated fluorine-free foams, *International FireFighter, pp41-44, Nov 2012 issue, MDM publishing*

Schaefer T, et al, Sealability Properties of Fluorine-Free Firefighting Foams, University of Newcastle, Australia, 2008, *Fire Technology Vol 44.issue 3 pp297-309* http://novaprd-lb.newcastle.edu.au:8080/vital/access/manager/Repository/uon:4815;jsessionid=E0140D586B0467E75B68993EBC83A1CA?exact=sm_subject%3A%22vapour+suppression%22

Environ International (2014) Assessment of POP Criteria for Specific Short-Chain Perfluorinated Alkyl Substances http://www.fluorocouncil.com/PDFs/Assessment-of-POP-Criteria-for-Specific-Short-Chain-Perfluorinated-Alkyl-Substances.pdf

Rotander (2015) Novel Fluorinated Surfactants Tentatively Identified in Firefighters Using LC-QTOF-MS/MS and a Case-control Approach, *Environ. Sci. Technol. 49(4) 2 pp2434-2442 DOI 10.1021/es503653n* http://pubs.acs.org/doi/abs/10.1021/es503653n

Glass et al (2014) Final report Australian Firefighters' Health Study, Monash University http://www.coeh.monash.org/downloads/finalreport2014.pdf

Gable (2014) Firefighting Foams: Fluorine vs Non-fluorine, UK Environment Agency, Fire Times Vol16/5 p80 Aug/Sept.2014 www.mmcpublications.co.uk

PFOS AND PFOA: SCREENING CRITERIA AND WHAT HEALTH INVESTIGATION LEVELS MIGHT LOOK LIKE

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INTRODUCTION

Criteria suitable for screening risks relevant to human health and ecological impacts are not currently available from Australian authorities for PFCs. Cardno has performed a literature review of available literature to compile a set of criteria suitable for screening PFOS which may be used in environmental site investigations. In addition, a set of soil screening criteria were derived based on available toxicological information to derive screening values equivalent to HIL in accordance with Australian guidance

BACKGROUND

Perfluorooctane Sulfonate (PFOS) is a perfluorinated compound (PFCs) which is a POPs as covered by the UN Stockholm Convention on Persistent Organic Pollutants (POP). The initial focus for PFCs has been on Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA) although other may be considered persistent. PFCs can be transported over long distances may also bioaccumulate. PFCs have been identified in water, sediments, plants, food produces and animals (in particular fish).

In humans, PFCs have been found predominantly in blood as some are known to bind strongly to plasma proteins. The main sources of PFCs for human exposure is the diet however PFCs are also present in surface coatings on fabric and consumer products. As a result of their widespread use PFCs are also found in sludge from waste water treatment plants. There are hundreds of chemicals that are classed as PFCs and little is known about their toxicology. This document is focussed on criteria for PFOS and PFOA; however, in a limited context they may be used as surrogates for other similar PFCs.

METHODS

Literature Review of Available Screening Criteria

A desktop literature review was conducted by Cardno to identify suitable screening criteria for PFC. The screening criteria adopted was dependent on a number of factors including the management goal, available toxicological data and an appropriate level of protection for various uses. They would typically be used in site investigations in order to do a preliminary assessment of the potential for risk from exposure to these compounds.

Derivation of Health Investigation Level (HIL)

HILs have not previously been prepared for PFC. Guidelines are available from other jurisdictions (e.g. USEPA 2009, MPCA 2009); however, these guideline values may not have been derived in a manner consistent with Australian guidance (e.g. limited exposure settings or exposure pathways included). Therefore, the methodology applied in Australian guidance (from NEPC 2013) was used to derive HIL. A set of parameter values were selected following a detailed literature reviewed.

RESULTS AND DISCUSSION

Cardno has developed a set of screening criteria for various exposure pathways for water, soil and biological tissues. This set of criteria is based on an exhaustive review of the literature and numerous projects that Cardno have been involved in involving PFCs. The exposure pathways covered include primary exposure pathways (such as drinking water, incidental ingestion of soil) and secondary exposure pathways which account for the bioaccumulation of PFCs. It is Cardno's experience that detection of PFC in water typically leads to collection of biological material to assess the potential for risk from secondary exposure pathways. A discussion of the screening criteria used by Cardno in environmental assessments will be provided. Note that the majority of criteria for secondary exposure pathways are available for PFOS only.

Criteria have also been derived by Cardno in a manner equivalent to HIL for soil using Australian methodology for four exposure settings (HIL-A to HIL-D). The residential HIL (HIL-A) derived for PFOS (4 mg/kg) was similar to the residential values derived by USEPA (6 mg/kg) and MCPA (2 mg/kg). Contribution to the HIL-A was significant from the consumption of fresh produce (68%) hence the HIL for other exposure settings (where consumption of produce is not an include pathway) are considerably larger (e.g. HIL-D for a commercial setting of 400 mg/kg). A thorough discussion of the parameter values and assumptions adopted in the derivation of HIL is included.

CONCLUSIONS

There are screening criteria available for PFOS and PFOA to assess various exposure pathways typically considered in Australian site investigations. This includes those secondary exposure pathways for PFOS/PFOA related to the bioaccumulative property of these PFCs. HIL were derived for PFOS and PFOA in accordance with Australian Methodology. A thorough discussion will be provided for set of screening criteria used by Cardno including their sources, assumptions in their derivations and the set presented on the HIL estimated (including parameter values used in their estimation) and the criteria available for use in screening for PFC in an environmental assessment.

REFERENCES

MPCA, (2009). Tier 1 and Tier 2 SRV Spreadsheet – updated for PFBA, PFOA and PFOS only. 6/09. Minnesota Pollution Control Agency.

NEPC (2013) Schedule B1. Guideline on Investigation Levels for Soil and Groundwater. National Environment Protection (Assessment of Site Contamination) Measure 1999. National Environment Protection Council (NEPC). Amendment Measure 2013 (No. 1).

USEPA (2009). Soil Screening Levels for perfluorooctanoic acid (PFOA) and perfluooctane sulfonate (PFOS). November 2009. U.S. Environmental Protection Agency.

ENVIRONMENTAL FACTORS AFFECTING THE SELECTION AND USE OF FIRE-FIGHTING FOAMS — A FIRE SAFETY PERSPECTIVE

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INTRODUCTION

Fire-fighting foam is a suppression agent known and used for preventing, controlling and extinguishing fires involving flammable liquids (Class B fuels). Firefighting foams are used in fixed and portable fire extinguishing systems as well as fire brigade apparatus.

In recent times there has been an increasing focus on environmental impacts related to the use of fire-fighting foam, often without due consideration of other key issues such as fire-fighting performance, firefighter safety and system compatibility.

Although environmental performance is important, failure to adequately consider the fire-fighting and system performance aspects of foams, may result in selection of a foam that is ineffective for the intended application. This can itself lead to greater environmental impacts resulting in longer extinguishment times, use of larger quantities of foam and water and the production of significantly greater quantities of fire water effluent which needs to be disposed.

DISCUSSION

The performance of firefighting foam is important in order to protect life, property and the environment. From a fire-fighting viewpoint, to be effective fire-fighting foams must:

- Cool the fuel surface
- Resist mixing with the fuel
- Resist attack or breakdown by the fuels (in particular, polar solvents)
- Suppress the release of flammable vapours
- Spread rapidly over the fuel surface
- Provide protection from re-ignition
- Be compatible with the foam proportioning and delivery equipment

The selection and use of different foam types should be determined with consideration of:

- Firefighting performance (including the impact on firefighter and community safety)
- Environmental performance
- Compatibility with the equipment or systems in which they are to be used
- Compatibility with existing foam concentrate in storage
- Potential tank/pipework corrosion
- Proportioning accuracy
- Cost

There is no such thing as an environmentally friendly foam. All fire-fighting foams have adverse environmental impacts. However, it must also be recognised that fires—especially those involving flammable liquids and other chemicals—have significant adverse environmental impacts in their own right. It is a general fire safety objective to extinguish a fire as quickly as possible. In achieving this objective there is a positive effect in terms of minimising risk to life safety, property, the environment and business interruption. Specifically, using the minimum possible quantity of foam and water, to control or extinguish the fire, is greatly beneficial in terms of reducing environmental impact by reducing the amount of fire water effluent to be managed post incident.

Significantly, fire-fighting foams containing fluorinated surfactants have valuable fire-fighting performance characteristics that improve fire fighter safety, provide increased fire-fighting effectiveness (vapour suppression, knockdown, burnback) which can significantly reduce the amount of foam required time to bring an incident under control and limit the associated environmental damage, as well as loss of life and property.

An incident at Caltex's Banksmeadow terminal in Sydney clearly demonstrated this. A large fuel spill had occurred and foam was used to provide vapour suppression and prevent ignition of the spill. It was found, that when using fluorine free foam (F3) effective vapour suppression (maintaining vapours levels below the fuels Lower Explosive Limit) was only achieved for 15-20 minutes before foam needed to be re-applied. When a fluoroprotein foam was later used, vapour suppression was achieved for a much longer, 90 minute, duration. Hence the use of a fluorinated foam can provide longer protection, significantly reduced frequency of reapplication and therefore potentially significantly reduce the amount foam and fire water effluent that needs to be managed post incident.

Hazardous facility managers and emergency services need the flexibility to use risk management principles to select the most appropriate equipment, tools and techniques appropriate to manage the particular risks at the facility in question. The risk management for these facilities must be considered holistically, from pre to post incident. Environmental risk management should not be based solely on considering post incident management.

Fluorine free foams do not provide a "silver bullet" solution to environmental problems associated with the use of fire-fighting foam. Use of F3 in some fire incidents could require the use of significantly larger quantities—potentially triple the amount—of both foam and water to manage an incident due to the inferior fire-fighting performance of the foam as evidenced by the Incident at Caltex's Banksmeadow terminal.

It is now known, as evidenced by AirServices Australia experience, even facilities which have changed to using F3, PFOS/PFOA contamination still exists many years later. As such, fire water effluent from any such sites should still be treated as a contaminated.

In our view, the QLD DEHP draft policy on the management of fire-fighting foam incorrectly assumes that if fluorine free foam (F3) has been used at an incident that there will be no contamination with fluorinated compounds in the fire water effluent. The experience at AirServices Australia sites demonstrates this is not necessarily the case. The draft policy also incorrectly assumes that the total societal risk resulting from an incident, up to the point the incident is controlled, will be the same regardless of the type of fire-fighting foam used. That is, the policy assumes that the fire-fighting performance of all foams at a given incident will be equal. This is NOT the case.

Proper management of fire water effluent is very important to minimise adverse environmental effects. Therefore, we believe environmental policies should focus on stipulating how the fire water effluent from an incident should be managed irrespective of the type of fire-fighting foam used. Testing of the effluent should be conducted to determine the appropriate method of treatment and disposal.

We endorse the approach, the United Kingdom EPA has implemented regarding the selection and use of fire-fighting foam; that is, allowing emergency services and hazardous facility managers to select and use the most appropriate foam concentrate to allow them to best manage their risks. The obligation to the environment then being that the resulting fire water effluent be appropriately managed. We recommend a similar approach be adopted in Australia.

PROGRAMMATIC APPROACHES TO IDENTIFICATION AND MANAGEMENT OF PORTFOLIOS WITH SITES POTENTIALLY IMPACTED BY PER- AND POLYFLUOROALKYL SUBSTANCES

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) have emerged in the environmental engineering arena as an unexpected and recalcitrant groundwater contaminant at many sites worldwide (Moody and Field, 2000; Rak and Vogel, 2009). Chemical characteristics of PFASs, such as high solubility relative to standards and relatively low sorption, result in potentially widespread impacts to groundwater systems. Very few sites have been extensively delineated, but among those with detailed characterization data, many indicate impacts to all media of interest, including groundwater, surface water, leachate, soil, sediment and air, as well as biological tissue samples. Recent sampling under the US Environmental Protection Agency's (EPA's) Unregulated Contaminant Monitoring Rule list #3 (UCMR3) reveals an occurrence rate in public drinking water supplies of 0.8% (USEPA 2015), which indicates numerous previously unidentified sources. Toxicological studies indicate that PFASs may be harmful, but insufficient information exists to determine carcinogenicity or derive reference doses that are required for risk assessment during site investigations to support remedial decision-making (Anderson, 2014). Potential Federal sites that may be impacted by PFASs-containing materials, specifically aqueous film forming foam (AFFF), include fire training areas, aircraft crash sites, petroleum tank farms, and petroleum firefighting locations, as well as chromium plating shops. As the regulations evolve over the coming years, it will be important to have an understanding of the sites where impacts to groundwater or other environmental media may be a concern.

METHODS

Federal agencies have employed a wide variety of approaches to identification and assessment of potential PFASs-impacted sites, ranging from case-by-case evaluation in response to direct regulatory inquiry, to enterprise-wide investigation of major installations in their portfolio. Examples include the US Department of Defence, specifically the Air Force, Navy, Army, and Air National Guard. Additionally, approaches taken by Fortune 100 multi-national corporations vary from programmatic approaches to individual site assessments. For the USAF, CH2M provided technical expertise performing Preliminary Assessments (PAs) of PFASs impacts from the use of AFFF at 82 US Air Force and Air National Guard installations. PAs involved preliminary interviews at the Command level, document review and research into the Air Force's usage history of AFFF. Site visits were conducted, involving interviews with Base personnel, including Fire Chief and environmental staff, review of aerial photographs, documents, drawings, and emergency response reports to identify locations with possible usage of AFFF. Similar to the USAF program, for the Australian Department of Defence, CH2M provided technical expertise and guidance performing desktop evaluation of possible PFASs impacts from the use of AFFF at 86 Department of Defence installations. Desktop evaluations involved document review and research into Defence's usage history of AFFF. The team also conducted interviews with Base personnel, including Fire Chief and environmental staff.

RESULTS AND DISCUSSION

Programmatic approaches employed by a number of organizations provide them with an overview of their portfolio of facilities and associated liabilities and potential risks to on-site and surrounding communities. Findings from these assessments indicate numerous potential AFFF release locations at almost every facility, including fire training areas, hangars, crash sites, spray irrigation fields, fire stations, and wastewater treatment plants. Recent sampling by the USAF of typical potential release locations at 10 bases indicates soil and groundwater detections at most locations, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (Long, 2015). Within the programs conducted by CH2M, the findings are not publically available at this time, but will be summarized verbally during the presentation. Overall, the findings suggest numerous locations where AFFF releases may have occurred, and where investigation is recommended, including soil and groundwater sampling.

CONCLUSIONS

Increasing regulatory and public interest in PFASs requires greater awareness from the regulated community. There is a high likelihood of stringent standards being promulgated in the future, and having an understanding of potential liability will allow facility owners to assess their potential risks and ensure they are not blindsided by the emergence of this group of chemicals. The programmatic approaches employed by the USAF and the Australian Department of Defence have identified a large number of locations where AFFF may have been released. Going forward, these organizations will be assessing whether releases actually occurred and whether those releases have resulted in impacted soil or groundwater above health advisory levels or other guidelines. In most situations, these compounds are not regulated at present so remedial actions may not be warranted. However, if in the future, the regulations are promulgated for PFASs, the organizations that understand the extent of their potential liability will be one step ahead of others who may find themselves scrambling to respond to newfound regulatory interest.

REFERENCES

Anderson, J., 2014, U.S. Air Force Programmatic Approach, Webinar - DOD: Emerging Contaminant Programs: Prioritization, Investigation and Remediation, Society of American Military Engineers, November 19, 2014.

Long, C., 2015, U.S. Air Force Investigation of Non-Fire Training Area AFFF Releases, REMTEC Conference, Westminster, Colorado, March 2-4, 2015.

Moody, C. A. and Field, J. A., 2000, Perfluorinated Surfactants and the Environmental Implications of Their Use in Fire-Fighting Foams. Environ. Sci. Technol. 34, 3864–3870.

Rak, Andrew and Catherine M. Vogel. 2009. Increasing Regulation of Perfluorinated Compounds and the Potential Impacts at Air Force Installations. Prepared for the U.S. Air Force. March.

U.S. Environmental Protection Agency, 2015, Unregulated Contaminant Monitoring Rule #3 Results, http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm#ucmr2013, June 2015

DECODING NEW FORMULATIONS OF AFFFS

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INTRODUCTION

Aqueous Film Forming Foams (AFFFs) containing fluoro-surfactants have been widely used to extinguish fuel and hydrocarbon fires. Unfortunately, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), previously formulated in AFFFs, were reported to enter ecosystems and food chains, accumulating in animal and human tissue, including the liver and blood. Concerns on the biological and environmental impacts of PFOS, coupled to the persistent nature, led to PFOS's phase out in the early 2000s and replacements have been developed, such as 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS)-, and 1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2FTS)-based fluoro-surfactants [1]. Although fluorotelomers are reported to be safe to environment, their fluoro-carbon skeleton still arise concerns on their degradability in the natural environment [2].

Due to patent and commercialisation issues, we currently do not know the exact formulations and ingredients in these formulations of AFFFs. Sometimes, we cannot directly detect ingredients of fluorotelomer (such as 6:2FTS and 8:2FTS) in the initial AFFF formulations. However, this does not mean these types of fluoro-carbon skeletons do not exist in the formulations. This is because they may be shielded by deriving or tailing with groups that might introduce some new functions. In this case, the derived groups, which usually contain non-fluoro-carbon skeletons, should be easily degraded in the natural environment. Consequently, the inert fluoro-carbon skeletons will become detectable in the form of degradation products, such as 6:2FTS and 8:2FTS.

To confirm the above hypothesis of derivation, we tested several formulations of AFFFs. We intentionally oxidised these AFFFs using chemicals (such as potassium permanganate). After 30 days of oxidisation, we measured the concentration of 6:2FTS and 8:2FTS from all 3 AFFF samples and compared the values with those prior to their oxidisation.

METHODS

All samples were diluted in Milli-Q water in centrifuge tubes (polypropylene) without any pre-treatment. 0.1 % $KMnO_4$ + 0.36 % HCl (w/w) was introduced into the tubes for the oxidisation process. Samples were analysed using astkCARE™ testing kit (CRC Care, Australia) [3] and HPLC-MS (Agilent 1260 + Quadrupole 6130) before and after the oxidisation.

RESULTS AND DISCUSSION

Fig.1 shows the quantitative results of 3 samples based on HPLC-MS data where 4 AFFF ingredients were targeted, including PFOS, PFOA, 6:2FTS and 8:2FTS, which were identified by their molecular ions (*m/z*). The concentrations of 6:2FTS and 8:2FTS experienced a significant increase after oxidisation, thus confirming the above hypothesis that fluorotelomer is produced during the oxidisation. 6:2FTS was estimated to be 1010 ppm (mg/L) for sample T after oxidisation, which was the highest for all 3 samples. Note this concentration may be smaller than the original formula because we could not guarantee that oxidisation took place at 100% of yielding rate.

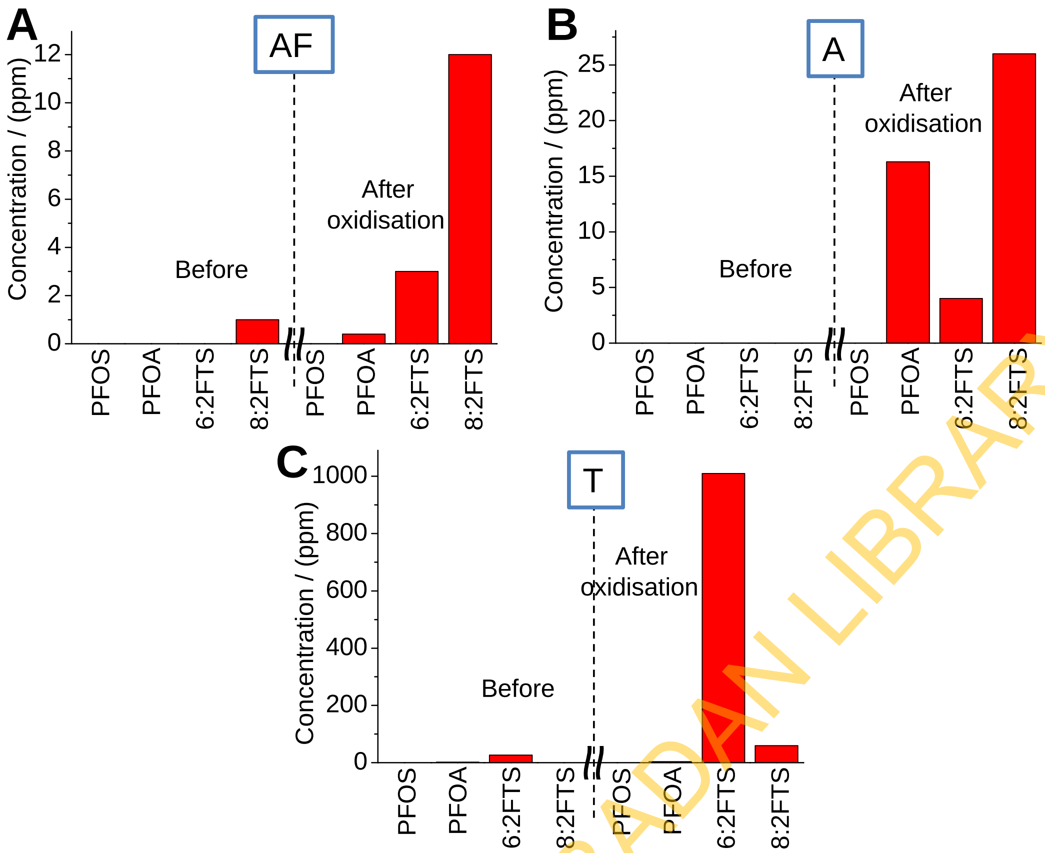

Fig. 1. HPLC-MS test results for sample AF (a), Sample A (b) and Sample T (c). The concentrations have been corrected using the dilution magnification to the values in the original formula without dilution.

CONCLUSIONS

We found significantly increased concentrations of 6:2FTS and 8:2FTS after oxidisation of AFFF formulations although these concentrations were not obvious before oxidisation. It is thus recommended to conduct environmental risk assessment for the formulations of AFFF, particularly in the long term when the fluoro-carbon skeleton resists natural degradation whilst the derived groups (most likely non-fluorinated side chains) are subjected to degradation.

REFERENCES

Cortina T, Korzeniowski S. 2008. Firefighting foams–Reebok redux. *Industrial Fire J(April 18–20)*.

Place BJ, Field JA. 2012. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environmental Science & Technology* 46:7120-7127.

Megharaj M, Ravendra N, Mercurio P. 2011. ANIONIC SURFACTANT DETECTION. In PCT I, ed, *AG01N2162FI* Vol AG01N2162FI Australia.

THE ROLE OF IRON IN THE FATE AND TRANSPORT AND REMEDIATION OF PERFLUOROALKYL SUBSTANCES

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INTRODUCTION

The goal of this presentation is to highlight the role of iron in the fate and transport, treatment, and potentially, in-situ remediation of perfluoroalkyl and polyfluoroalkyl substances(PFAS) [Buck, et.al, 2011]. These substances, a subset of fluorinated compounds, are anionic surfactants that have been widely used in industrial and domestic applications, including fire fighting with aqueous film forming foam (AFFF). Most commonly PFAS include the long-chain compounds perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), compounds that have captured the interest of regulators, environmental scientists, and the public because of their toxicity and tendency to bioaccumulate creating potential risk to human health and the environment. Iron is one of the most abundant rock-forming elements in the earth's crust and is found to impact the fate of PFAS in the both the native subsurface and in engineered systems.

This study presents an overview of chemical interaction between PFAS and iron oxides in the aqueous phase and the implications for fate and transport and remediation at contaminated land sites.

METHODS

PFAS are strong acids that dissociate to anionic form in aqueous systems. Therefore, it is expected that PFAS will adsorb preferentially to positively charged surfaces like aluminium and iron oxides through electrostatic or covalent bonds. In fact, Gao and Chorover established that PFOA formed inner sphere Fe-carboxylate complexes by ligand exchange on hematite (Fe_2O_3) and the PFOS sulfonate group forms outer sphere complexes and possibly hydrogen bonding on the mineral surface [Gao and Chorover, 2012].

To evaluate implications for fate and transport in soil and groundwater, data from a site impacted with PFAS was assessed for evidence of adsorption processes with naturally-occurring iron and aluminium oxides and oxyhydroxides in rock and mineral formations. Undisturbed samples of soil and groundwater were collected using in-situ vertical profiling techniques, and tested for PFAS and geochemical parameters.

Iron has long played a role in the remediation of organic and inorganic contaminants. Iron salts have been commonly used in the coagulation, precipitation, and co-precipitation of anionic compounds in water treatment systems. One particularly effective set of compounds are iron oxyhydroxides formed from the oxidation of ferrous or ferric iron under slightly alkaline conditions. Iron oxyhydroxides, also known as Hydrous Ferric Oxides (HFO), have an amorphous structure with high surface area and positive charge. The in-situ formation of HFO under natural or engineered conditions has been effective in binding anionic compounds, with potential to bind and precipitate PFAS.

To evaluate implications of HFO adsorption for remediation, laboratory proof-of-concept tests were performed. Batch adsorption tests consisted of an aqueous sandy soil mixture spiked with various concentrations of PFOS and PFOA. The soil/water mixture was then treated with a chelated-iron solution and hydrogen peroxide for the formation of HFO.

RESULTS/CONCLUSION

The initial site investigation results indicate a preferential concentration of PFAS in soil and groundwater in geological intervals containing iron and aluminium oxyhydroxides.

The preliminary results of the proof-of-concept batch tests indicate a 20-percent reduction in PFOS compared to a control batch. Critical parameters that affect the adsorption process include pH, solution ionic strength, and contact time.

The processes involving adsorption of PFAS on iron oxides/oxyhydroxides should be a consideration in assessing sites with impacted soil and groundwater and is likely a significant factor in understanding the fate and transport of PFAS in the environment. These processes have potential for adaptation to the remediation of PFAS both aboveground and in-situ. In particular, the in-situ formation of iron oxyhydroxides is worthy of further development.

REFERENCES

Buck, et.al, 2011. Robert Buck, James Franklin, Stefan PJ Van Leeuwen, *“Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins,”* Integr Environ Assess Manag. 2011 Oct; 7(4): 513–541, published online 2011 Jul 25. doi: 10.1002/ieam.2582011.

Gao and Chorover, 2012. X Gao and Jon Chorover, *“Adsorption of Perfluorooctanoic Acid and Perfluorosulfanoic Acid to Iron Oxide Surfaces as Studied by Flow-Through ATR-FTIR Spectroscopy,”* Environ. Chem. 9, 148–157, http://dx.doi.org/10.1071/EN11119. April 2012.

PROFICIENCY STUDY OF LABORATORIES ANALYSING PFOS AND PFOA IN WATER AND SOIL

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INTRODUCTION

Per and poly fluoralkyl substances (PFASs) have been widely used in the past in firefighting Aqueous Film Forming Foams (AFFFs). Perfluorooctane sulfonic acid (PFOS) and its salts are listed in appendix B of the Stockholm convention, which limits the production and transport and disposal of these compounds, Australia is a signatory to the convention. The characterisation of PFAS contaminated sites, and subsequent remediation, relies on accurate measurement of these compounds in environmental matrices such as soil and water. A recent review (CRC CARE, 2013) of emerging contaminants identified a lack of Australian infrastructure to ensure quality and comparability of PFAS measurements, particularly Proficiency Testing (PT). CRC CARE has funded this project to provide a suitable PT scheme in collaboration with National Measurement Institute (NMI) and EPA Victoria. NMI is an accredited PT provider according to ISO 17043 (ISO/IEC, 2010).

METHODS

A review of current international regulatory limits and environmental concentrations was undertaken to determine target concentrations for the PT samples. Four samples were prepared – two soil and two water samples. In each matrix one sample was incurred and one spiked by the study coordinator. Incurred soil was air dried, foreign material was removed, followed by grinding by cross beater mill and thoroughly mixed, and diluted with PFAS-free soil, mixed again, then dispensed into sample aliquots (S1). The PFAS-free soil was spiked with known amounts of PFOS and Perfluorooctanic acid (PFOA) and mixed again before dispensing into sample aliquots (S2). The incurred water was mixed by stirring and dispensed into sample bottles (S3). The PFAS-free water was spiked with known amounts of PFOS and PFOA, mixed and dispensed into sample bottles (S4). The sample containers used for both soils and waters were chosen to reduce contamination or absorbance of the target analytes. The homogeneity of all test materials was confirmed by analysis of eight units elected at random and analysed in duplicate. The homogeneity studies were conducted as described in the International Protocol (Thomson, 2006). Soil samples were extracted by tumbling with solvent, and water samples extracted by solid phase extraction (SPE) with solvent elution. After solvent evaporation and filtration, the extracts were analysed by Liquid Chromatography Tandem Mass Spectrometry (LCMSMS), with two mass transitions monitored for each compound, and quantitation using the isotope dilution method.

The samples were dispatched to eleven testing laboratories, made up of nine commercial (five accredited) and two academic laboratories, with two international laboratories participating (New Zealand, Taiwan). The laboratories analysed the samples using routine test methods and ten submitted results and nine uncertainty estimates for each sample, along with their answers to a questionnaire about analytical methodology. The results were collated and participants' performance assessed using z-scores and E_n-scores. A concluding workshop was then held to discuss the results of the study with participants.

RESULTS AND DISCUSSION

The incurred samples were chosen to provide ‘real world’ samples in terms of matrix and weathering of the target analytes. An aspect of this is the presence of both linear and branched PFOS isomers which are present in the technical mixtures of PFOS used in industry. There have been anecdotal suggestions that testing laboratories may not report branched isomers in the same way and that this could create differences in analytical results for the same sample submitted to different laboratories. To address this issue, both the incurred soil and water contained linear and branched isomers and the laboratories were instructed to calculate results for linear and branched isomers using linear calibration standards, which was generally performed satisfactorily. The assigned value was the consensus (robust average) of participant results. There is good agreement between the assigned value, the formulated (spiked) concentration and the results of NMI homogeneity testing. Results for samples S2 (spiked soil) and S4 (spiked water) are presented in Figures 1 to 4.

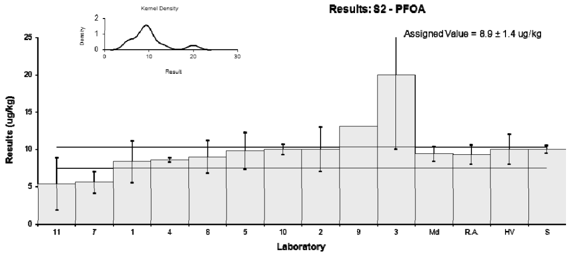

Fig. 1. Sample S2 spiked soil PFOA

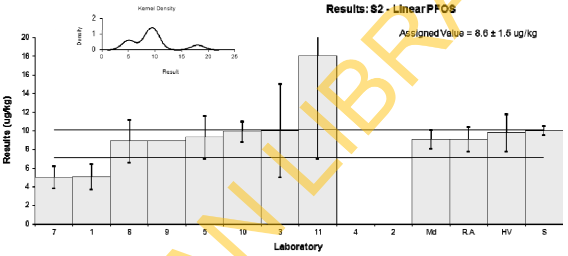

Fig. 2. Sample S2 spiked soil linear PFOS

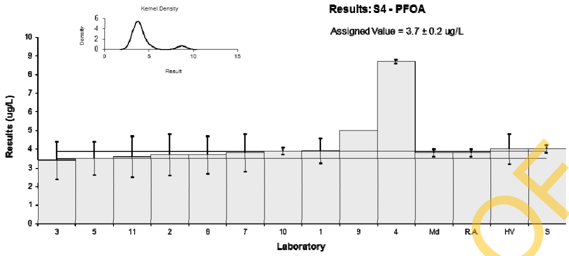

Fig. 3. Sample S4 spiked water PFOA

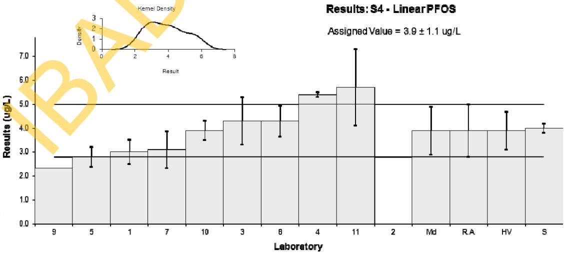

Fig. 4. Sample S4 spiked water linear PFOS

CONCLUSIONS

This study has been a valuable tool to improve the ability of Australasian chemical testing laboratories to accurately measure PFOS and PFOA in environmental soils and waters. Overall the laboratories performed well with an average of 79% satisfactory z-scores and 74% satisfactory E_n-scores. This reflects that PFOS and PFOA analysis is generally only being undertaken by experienced laboratories with advanced instrumentation. However only two laboratories submitted satisfactory results for all analytes and matrices, indicating some variance of results, especially for PFOS. The majority of laboratories were able to report linear and branched PFOS combined as total PFOS. The participant workshop enabled the laboratories to discuss methodology differences that may have contributed to the differences.

REFERENCES

CRC CARE 2013, Analytical methods for priority and emerging contaminants – a literature review, CRC CARE Technical Report no. 24, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia

ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing, (2010) ISO, Geneva.

Thomson M., Ellison S.L.R. and Wood R., 2006, The international harmonised protocol for proficiency testing of (chemical) laboratories, Pure Appl. Chem. 78, 145-196.

TREATMENT OF PFCS IN SOILS, SEDIMENTS AND WATER

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INTRODUCTION

Emerging contaminants PFOS (perfluorooctane sulfonate), PFOA (perfluorooctanoic acid) and other perfluorinated compounds (PFCs) are toxic, persistent and bioaccumulate in the environment. As a result, in 2009 PFOS was included in the Stockholm Convention on persistent organic pollutants.

Fire-fighting foams are the most commonly known source of PFCs (also known as aqueous film-forming foams - AFFFs). Other sources of PFCs include cookware, water repellents, fabric protectors, carpets and many other common industry products.

TREATMENT OF PFCS

Recent commercial-scale treatment trials conducted by Enviropacific on PFC impacted soils, sediments and water from two sites in Australia have demonstrated highly effective chemical immobilisation of all 20 commonly observed PFC analytes, with significant reductions of the major PFCs, and all minor PFCs reported as below laboratory detection limits.

Water treatment

Full-scale water treatment of PFCs at RAAF Williams Point Cook, VIC was recently completed with over 16 million litres of water treated, which will be presented. The technology and equipment are well established, with the water treatment equipment designed to treat PFC contaminated water at rates of up to 10 L/s.

Treatment trials were also conducted on water derived from wash water storage at a fire training facility and a summary of these results is shown in Table 1.

Table 1. Treatment trial results for PFC impacted water. (Note: other PFCs in the suite of 20 commonly observed compounds were reduced to non-detect levels.)

	PFOS	PFOA
Untreated (µg/L)	57.1	0.53
Treated (µg/L)	<0.02	<0.02
% reduction	>99	>96

Soil and sediment treatment

Treatment trials were recently conducted on sediments collected from a fire training facility that were derived from wash water storage, and a summary of these results is shown in Table 2. A highly effective adsorbent reagent was utilised in the trials and optimised to minimise its usage.

A field-scale treatment trial on PFC impacted soil at another site is also currently being undertaken and progress results for this trial will be presented.

Table 2. Treatment trial results for PFC impacted sediment. (Note: other PFCs in the suite of 20 commonly observed compounds were reduced to non-detect levels.)

	PFOS*	PFOA*
Untreated (µg/L)	47.6	1.85
Treated (µg/L)	<0.02	<0.02
% reduction	>99	>99

*Australian Standard Leaching Procedure (ASLP-acetate)

The equipment used for the full-scale soil and sediment treatment process is Enviropacific's Hitachi Soil Recycler, which is a track-mounted pug mill specifically engineered to provide high shear mixing for treatment of contaminated soils and sediments. The machine efficiently adds a variety of reagents with high accuracy to ensure adherence to specific immobilisation approvals and conformance.

CONCLUSION

This paper will present results from bench-scale and field-scale soil, sediment and water PFC treatment. The treatment techniques, which will be discussed, are based on chemical treatment and adsorption and are straightforward, cost-effective and able to be readily up-scaled to commercial application using mobile treatment equipment.

COMBINED GENOTOXIC EFFECT OF ARSENIC, CADMIUM, CHROMIUM AND FOUR POLYAROMATIC HYDROCARBONS

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INTRODUCTION

The joint effects of organic and inorganic contaminants as beyond the binary mixtures have not been well characterised. In this study we evaluated the combined genotoxicity of mixtures of PAHs and heavy metal/loids containing benzo[a]pyrene (B[a]P), naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), As, Cd and Cr using the in-vitro micronucleus test in a human liver cell line (HepG2 cells). The activation of aryl hydrocarbon receptor (AhR) by single and mixed PAHs was also measured. This study contributes to a better understanding of combined effects of mixtures containing both organic and inorganic contaminants for health risk assessment purposes.

METHODS

Human hepatocellular carcinoma cell line, HepG2 cells were cultured at 37°C under 5% CO_2. Solutions of B[a]P, Nap, Phe and Pyr were prepared in DMSO and the mixture was made by mixing equal volume of each solution. Aqueous solutions of sodium arsenite, cadmium chloride and potassium dichromate and the mixture were prepared similarly. The exposure experiments included single and mixed compounds of PAHs and heavy metal/loids. Mitomycin C (MMC, 2 µM) was used for the positive control for metal/loids. DMSO and H2O were used as the negative control. Cytotoxicity was measured by MTS assay. Micronucleus (MN) frequency was determined by cytokinesis-block micronucleus assay which also provided cytostasis (toxicity) data. Chemical treatment and MN test were performed according to published methods (Fenech 2007, OECD 2014). HepG2 cells were transfected with reporter plasmid, pGreen1.1, using TfxTM-20 regent (Promega: E2391) for the establishment of a stable transfected green fluorescent protein reporter assay for the measurement of AhR activation.

RESULTS AND DISCUSSION

Cytotoxicity (MTS assay) dose-response relationships of individual compounds were established from which doses for the mixture interaction studies were selected. The results indicated that individual and mixed Nap, Phe and Pyr did not induce significant micronucleus (MN) frequencies. However, PAHs mixture containing B[a]P and B[a]P alone caused significant but similar level of MN frequencies. The same pattern was found in the AhR induction. Individual metal/loid induced significant cytostasis and MN formation of which Cd was found to be the most potent inducer. Mixture of metal/loids caused higher frequency of MN suggesting a possible additive effect among the metal/loids tested. In addition, binary mixture of metal/loids and B[a]P, namely As/B[a]P, Cd/B[a]P and Cr/B[a]P increased MN formation. Mixture of Cd and B[a]P induced the highest level of MN. Exposure of cells to the mixture containing B[a]P and Cd/Cr/As at lower concentration (0.25 µM) resulted in significant MN frequency, the level of which was equal to that by Cd/B[a]P at 1.0 µM.

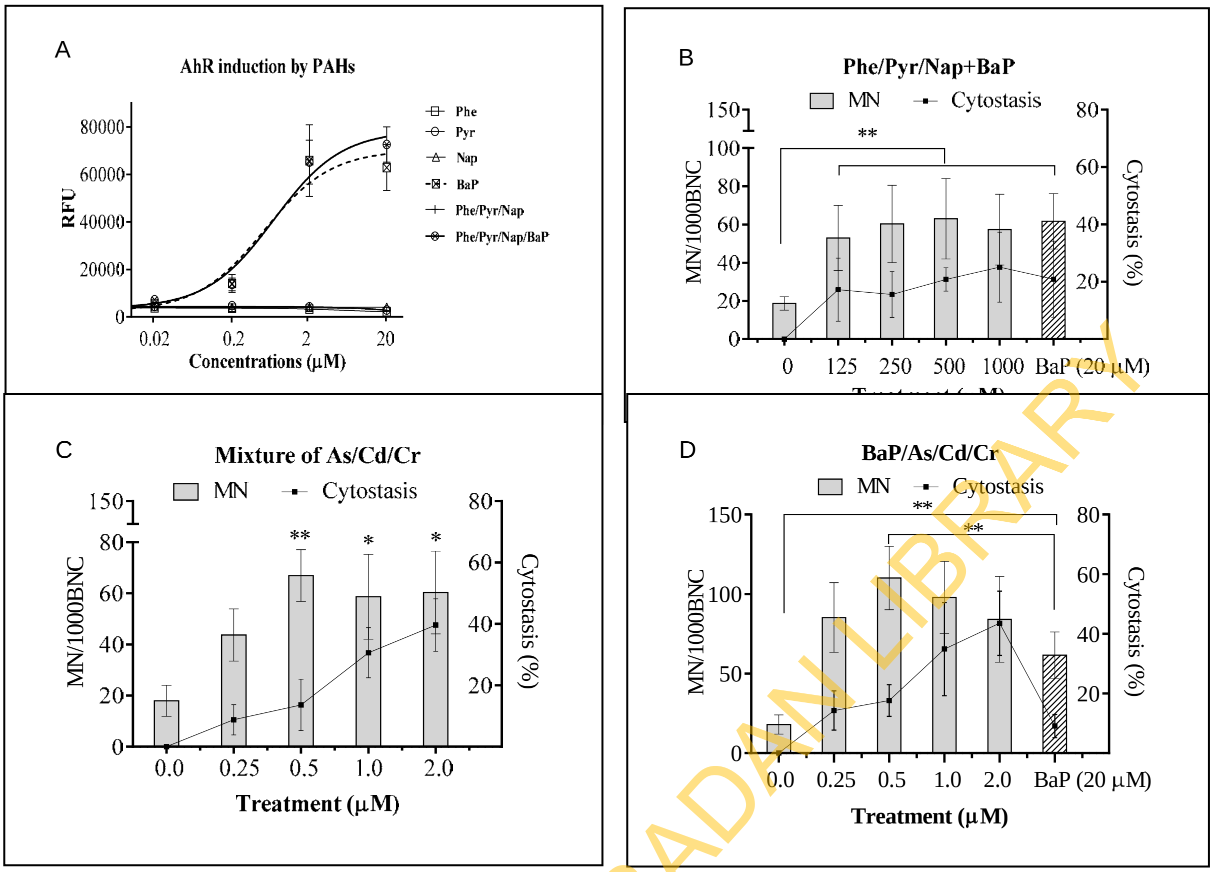

Fig. 1. Induction of AhR in HepG2 cells exposed to single or mixed PAHs (A); Micronucleus (MN) frequency per 1000 binucleate cells (BNC) and cytostasis caused by mixed PAHs (B); mixed metal/loids (C); and B[a]P and metal/loids. Where * indicates *p*<0.05; ***p<0.01.*

CONCLUSIONS

We compared single and mixed three heavy metal/loids and four PAHs for their genotoxicity in HepG2 cells. Based on the results, we propose that the combined potency of DNA damage caused by the exposure to PAHs mixture(s) of B[a]P, NaP, Phe, and Pyr is dependent on the compound with the most potency in the mixture which is B[a]P. For the mixture(s) of heavy metal/loids and PAHs (Cd/Cr/As/B[a]P), an additive effect may exist in a compound- and concentration-dependent manner. The compounds with the highest potencies of genotoxicity in the mixture seem dominant as the drivers in the final combined genotoxic effect of PAHs and heavy metal/loids. Understanding the interaction effect and identifying the dominant contaminant(s) in mixture exposure will inform a more refined risk assessment.

The project was funded by CRC Contamination Assessment and Remediation of the Environment (CRC CARE, Grant No. 3.1.01.11-12). Entox is a partnership between Queensland Health and the University of Queensland.

REFERENCES

OECD (2014) Test No. 487. In Vitro Mammalian Cell Micronucleus Test. *OECD Guidelines for the Testing of Chemicals*. Section 4: Health Effects.
Fenech, M. (2007) Cytokinesis-block micronucleus cytome assay. *Nat Protoc*. 2: 1084-1104.

EVALUATING CHROMIUM SPECIATION IN GROUNDWATER TO GUIDE RISK ASSESSMENT AND REMEDIATION DECISIONS

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INTRODUCTION

The fate, transport and environmental and health impacts of metals including chromium are highly dependent on the species in which the metal is present in the environment (e.g. McNeill et al., 2012). As part of the early stages of environmental assessment, chromium is typically the metal analysed for its specific species (i.e. Cr(VI) vs total dissolved Cr). However, even when Cr(VI), which is considered a carcinogen, results are available, assessing the likely migration and fate of Cr(VI) in aquifers can be challenging.

This abstract presents a summary of the value of assessing geochemical and hydrogeological conditions as part of site assessments so as to better understand the likely fate of Cr(VI) in groundwater environments. This provides essential information from which to develop appropriate risk-based decisions regarding the extent of remediation and/or management required to protect human health and the environment.

BACKGROUND

The study presented here investigated Cr(VI) impacts to groundwater associated with a former timber treatment chromated copper arsenate (CCA) operation in Australia. Both shallow groundwater in a perched aquifer (considered to be associated with former site operations) and in the deeper regional bedrock aquifer were assessed, and Cr(VI) was found to be present in both zones. A downward hydraulic gradient was present between the two water bearing units, so it was important to assess the extent to which Cr(VI) transport associated with seepage from the perched to the deeper aquifer had or was likely to occur. Additionally, since both the perched and regional water table were impacted, assessing the potential for Cr(VI) to migrate laterally beyond the site was important.

METHODOLOGY

Groundwater monitoring wells were drilled to either the perched or underlying bedrock aquifer and bedrock cores were collected from several locations. Solid samples from each zone were analysed for potential chromium reductants including ferrous iron, sulfide, and total organic carbon (TOC) while groundwater samples were analysed for pH, redox conditions, major ions, speciated Cr, and other redox sensitive parameters. The solid and aqueous geochemical data were analysed together with logs, aquifer parameters and groundwater elevations to develop a conceptual site model (CSM) that integrated physical and chemical conditions. This included development of a 3-D geological model and a geochemical model and, following assessment against the criteria adopted for groundwater at the site, allowed appropriate remediation and management measures to be developed.

RESULTS AND DISCUSSION

Across the site, the regional water table occurred in competent bedrock with perched water present in overlying sediments above weathered bedrock. The weathered bedrock was considered to act as a semi-confining unit allowing some leakage to the underlying bedrock aquifer. Concentrations of Cr(VI) in groundwater from both the perched zone and regional aquifer were delineated away from the source area, indicating that attenuation is occurring in these units.

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Geochemical analysis indicated that in the perched zone, weathered bedrock and competent bedrock sulfur was present typically as sulfate minerals. Based on redox conditions, iron in solids was likely to be present as ferric iron (Fe[III]). Consequently, neither of these species was likely to facilitate reduction of Cr(VI) to Cr(III). By contrast, TOC concentrations in the perched zone were substantial, ranging from 200 to 300 mg/kg, indicating that organic matter in this zone had the potential to reduce Cr(VI). TOC concentrations in solid samples from the unweathered bedrock aquifer were below the limit of reporting.

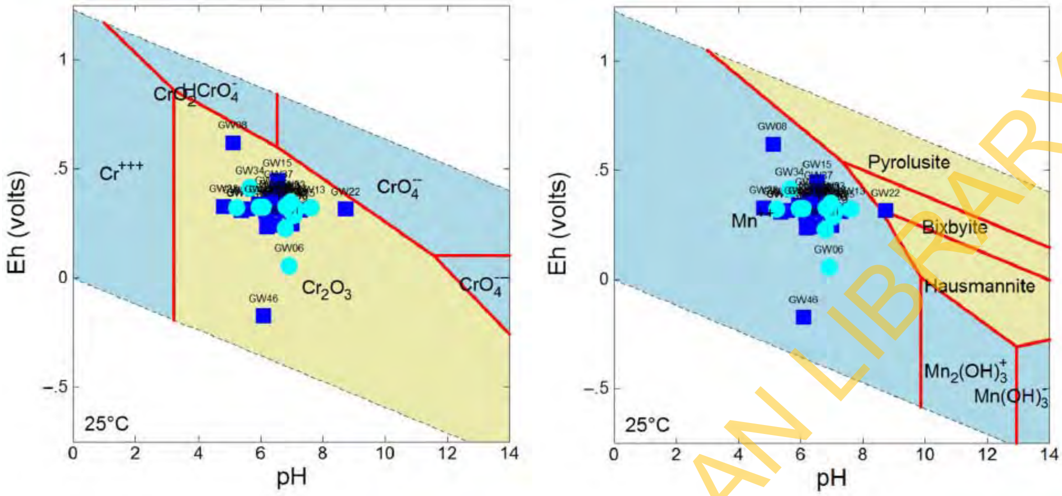

Figure 1: Eh-pH diagrams for Cr and Mn in groundwater (squares, perched aquifer; circles, bedrock aquifer)

The potential for Cr(III) to be oxidised to Cr(VI) through manganese oxides (e.g. Richard and Bourgh, 1991) was also assessed by geochemical modelling using Geochemist's Workbench. Both pH-Eh activity diagrams (Figure 1) and calculations of mineral saturation indices indicated that pyrolusite was not likely to be present as a reactive mineral in the groundwater system and consequently Cr(III) would be unlikely to be oxidised to Cr(VI).

pH conditions in groundwater were circum-neutral, and Eh values were low. However, Fe(II) and sulfide concentrations in groundwater were also low, indicating that these parameters would be unlikely to provide capacity to reduce Cr(VI). TOC was present in groundwater at concentrations of 1-10 mg/L indicating that, if the TOC were biologically available, the groundwater would have some Cr(VI) reducing capacity, consistent with the stability field for Cr(III) inferred from Eh-pH stability diagrams (Figure 1).

CONCLUSIONS

The solid phase and groundwater geochemical assessment conducted at this site indicated that conditions are present that can reduce Cr(VI) to Cr(III) in the receiving groundwater environment. This has strengthened arguments based on more standard assessment techniques which have delineated impacts at the site, and has allowed zones to be clearly identified where potential risks to receptors are present; assessment strategies have been developed to further quantify those risks. The assessment has also provided a clear rationale for designing a targeted, and less extensive, monitoring program to confirm that conditions remain stable or improve at the site where Cr(VI) impacts remain in groundwater,

REFERENCES

McNeill, L., McLean, J., Edwards, M. and Parks, J, 2012. State of the science of hexavalent chromium in drinking water, Water Research Foundation, Updated May 2012.

Richard, E and Bourgh, A, 1991. Aqueous geochemistry of chromium: a review. Water Resources, 25, 7, pp. 807-816.

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RAPID RISK ASSESSMENT TO ADDRESS PUBLIC HEALTH CONCERNS REGARDING POTENTIAL EXPOSURE TO ANTIMONY

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INTRODUCTION

Faced with strong community concern, media interest and a two-week timeframe, how would you approach deriving an answer to "*Is there immediate concern of adverse health effects to the community due to antimony exposure?*"

This was the case when Golder Associates Pty Ltd (Golder) was engaged as an independent expert by a Reference Group of State Government Agencies. Community concerns regarding antimony exposure relating to local mine operations arose following elevated antimony concentrations being reported in the urine of local residents (adults and children). Because of the rarity of exposure, the reference range for antimony in urine or biological exposure indices are not well defined making the direct assessment of results challenging. The suspected environmental cause (local mine activities) indicated that the urine results did require further assessment. The quick response time meant a standard Human Health Risk Assessment (HHRA) could not be completed and a different approach needed to be developed. Golder completed a *rapid HHRA*, involving a rapid monitoring program and a streamlined approach to assessing the potential risk. The rapid HHRA approach focused on understanding antimony intake routes and associated health risk.

METHODS

The assessment involved a multi-levelled approach, comprising the following steps:

- Development of an objective approach to answer: "Does an immediate health risk to the community exist from antimony exposure?"
- Field work design to support the rapid assessment conceptual model.
- Initial screening of antimony data collected during the rapid monitoring program (soil, tank water and air results) against adopted assessment guidelines and criteria.
- Calculation of an estimated Daily Antimony Intake (EDI) for identified residents (amount of antimony potentially taken up by a person from tank water, soil and air) and comparison of the EDI to a regulatory value for Tolerable Daily Intake (TDI).
- Further assessment of the TDI exceedences using a Margin of Exposure (MoE) method**.** The MoE method is not commonly used in the assessment of human health risks posed by contaminants in the environment. This step involved understanding the No Observed Adverse Effect Level following repeated exposure to antimony and calculating a margin between the amount of antimony known to cause adverse health effects and the EDI. Immediate concern was judged as a margin of less than 100 fold.

RESULTS AND DISCUSSION

Antimony in tank water exceeded the Australian Drinking Water Guideline at all of the tested residences (33 properties). At 6 of 33 properties investigated the estimated calculated EDI exceeded the TDI for young children (< 3 years of age). This indicated that a potential risk existed for children in the community. However, at these properties the MoE was calculated as > 100. Therefore, it was judged that the community was not at immediate concern of adverse health effects. This judgment could not have been made without the use of the MoE method. It allowed the situation to be appropriately managed within the rapid timeframe required and now a full HHRA can be undertaken, allowing a year for data collection.

SOIL CONTAMINATION AND RISK ASSESSMENT AT HOUNSLOW HEATH EX-LANDFILL SITE IN LONDON, UK

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INTRODUCTION

Land contamination poses potential health risks to human and ecosystems, and has major economic, legal and planning implications for society (Hou and Al-Tabbaa, 2014). Hounslow Heath is a Site of Importance for Nature Conservation in the UK. Significant past uses of the land include long-standing military activities and extensive mineral excavation. To ensure the land is safe and suitable for human use and development, the site was investigated for the burden of persistent organic pollutants i.e. polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). PCBs and PAHs are classified as probable human carcinogens, in addition to their known adverse effects on the human immune, reproductive, nervous and endocrine systems (Winneke et al., 2002). This talk will cover the contamination intensity and spatial variation of PCBs and PAHs in the ex-landfill site, compare the contamination levels of PCBs and PAHs with relevant guideline values, and assess the uncertainty from sampling and analytical procedures and its impact on risk assessment.

METHODS

Chemical Standards

The standard solution containing 16 PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene was obtained from Supelco, UK. A deuterated internal standard (IS) mixture containing acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} was also obtained from Supelco. PCB congeners (18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, 194, 209) were obtained from Supelco, while ^{13}C-labelled IS (CB-52, CB-153, CB-209) was purchased from Cambridge Isotope Laboratories, USA.

Soil Sampling

The Hounslow Heath contaminated site was surveyed in 2012 by taking samples in a 25600 m^2 area. Within the sampling area, a total of 25 sites were chosen, where a duplicate auger sample was taken 4 m either north or south from the original locations using a balanced sampling design (Fig. 1a). Soil samples were characterised for elemental composition and specific surface area.

Sample Extraction and Analysis

PAHs and PCBs in soil samples were extracted by ultrasonication (Zhou et al., 2014). Soil samples (10 g dry weight) were mixed with copper granules, ashed sodium sulphate, 500 ng of IS and 50 ml of ethyl acetate or dichloromethane for PCBs and PAHs, respectively. The solvent extracts were reduced to 1 ml under rotary evaporation and cleaned-up by passing through columns containing silica: deactivated alumina. All sample extracts were analysed by gas chromatography-mass spectrometry.

RESULTS AND DISCUSSION

Most PCB congeners were detected in soil samples. Total PCB concentration was between 7.7 ng/g and 368 ng/g on a dry weight basis. Of all the samples, 40% of which showed a ∑PCB value which is significantly higher than the target value (20 ng/g), suggesting that PCB contamination levels in Hounslow Heath may have caused damage to the soil organisms. ∑PAH concentrations in soil was from 3772 ng/g to 121 µg/g. The concentrations varied widely between sites. PAHs were detected in all soil samples. A large proportion of the soil PAH burden was from higher molecular mass compounds, and in particular 5-ring compounds which accounted for 37-52% of total PAH burden in the soil samples. To assess potential environmental impacts of PAHs in soil, the concentrations of PAHs in soils were compared with the effects-based guideline values proposed by the US National Oceanic and Atmospheric Administration. Ten sites in Hounslow Heath showed a ∑PAH concentration higher than the effects-range medium (ER-M) value (45000 ng/g). Further, the remaining sites with the exception of one site showed total PAH concentrations greater than the effects-range low (ER-L) value (4000 ng/g). Individual compounds such as fluoranthene and pyrene often exceeded their ER-M values of 5100 ng/g and 2600 ng/g, respectively.

The measurement uncertainty is often neglected in contaminated land investigations. It can be estimated from the analysis of variance using the data from the balanced design of duplicate samples and analyses (Boon and Ramsey, 2012):

$$s^2_{meas} = s^2_{samp} + s^2_{anal} \qquad (1)$$

where s_{samp} is the standard deviation from sampling, s_{anal} is the standard deviation from analysis, and s_{meas} is the standard deviation of measurement. The percentage variance from the sampling, analysis and geochemistry is shown in Fig. 1b, demonstrating the analytical procedures to be robust. However, the measurement uncertainty is over 70% which is highly significant and needs to be considered in the risk assessment of contaminated land.

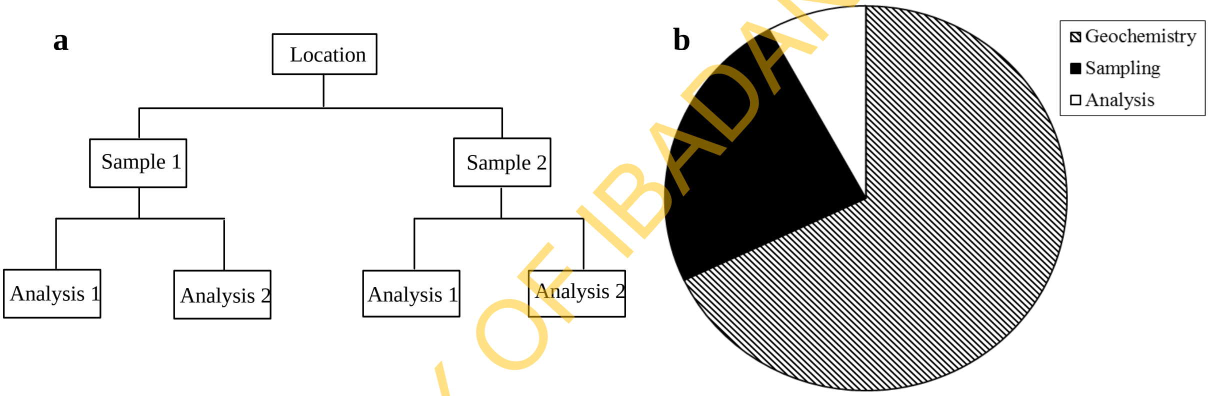

Fig. 1. **(a) Balanced sampling design, (b) Percentages of the total variance contributed by the analysis, sampling and geochemistry for PAHs.**

CONCLUSIONS

A balanced sampling design was adopted for the determination of PCBs and PAHs in soil samples from an ex-landfill site in London, UK. Total PCB concentrations in soil varied between 7.7 ng/g and 368 ng/g, while total PAH concentrations varied from 3772 ng/g to 121 µg/g, with 40% of sites exceeding relevant threshold values. Crucially, the uncertainty from sampling and analysis was estimated, demonstrating its importance in the classification and decision-making of contaminated land.

REFERENCES

Boon, K.A. and Ramsey, M.H. (2012) Judging the fitness of on-site measurements by their uncertainty, including the contribution from sampling. *Sci. Total Environ.* 419:196-207.

Hou, D. and Al-Tabbaa, A. (2014) Sustainability: A new imperative in contaminated land remediation. *Environ. Sci. Policy* 39:25-34.

Winneke, G., Walkowiak, J. and Lilienthal H. (2002) PCB-induced neurodevelopmental toxicity in human infants and its potential mediation by endocrine dysfunction. *Toxicol.* 181/182:161-165.

Zhou, J.L., Siddiqui E., Ngo, H.H. and Guo, W. (2014) Estimation of uncertainty in the sampling and analysis of polychlorinated biphenyls and polycyclic aromatic hydrocarbons from contaminated soil in Brighton, UK. *Sci. Total Environ.* 497-498:163-171.

ZERO-VALENT IRON MATERIALS FOR ENVIRONMENT RESTORATION — A RELOOK AT THE UNMODIFIED, CATALYZED, AND SULFIDED IRON

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INTRODUCTION

Chlorinated ethenes, including PCE and TCE, are the most prevalent contaminants at the US superfund sites. Although zerovalent iron (ZVI)-mediated reductive dechlorination is an important abiotic degradation pathway for chlorinated ethenes, the performance of ZVI under field conditions has been comprised by its relatively slow reaction rates in the absence of catalyst additives and its tendency to undergo surface passivation. Extensive studies have established that incorporating a small amount of catalyst metal, most commonly Ni or Pd, onto the iron substrate can lead to vast improvements in dehalogenation rates and minimal production of undesirable intermediates. Nonetheless, the bimetallic iron is prone to catalyst deactivation, and rapid iron corrosion in the presence of Pd in the aqueous environment raises serious concerns with regards to particle longevity and remediation efficiency [1,2]. More recently, treatment of nano-scale iron with reduced sulfur chemicals have been explored. Compared to the unmodified iron, addition of reduced sulfur precursors during laboratory nanoparticle synthesis created particles with significantly enhanced dehalogenation reactivity [3]. However, the role of sulfur in promoting the activity of iron has not been established and the general applicability of sulfidation treatment to various types of ZVI used in the remediation industry has not been assessed. Herein, the authors will present their recent findings on the surface reactivity of different iron materials, highlighting the effects of groundwater chemistry on the dehalogenation activity of bimetallic iron, and the potential of sulfidation treatment as an alternative route to increase ZVI materials' reactivity and field performance.

METHODS

The ZVI materials used in this study include laboratory synthesized monometallic and bimetallic iron nanoparticles as well as commercially available iron materials. Effect of groundwater matrix on bimetallic particle deactivation was assessed by exposing fresh bimetallic particles to aqueous solutions amended with various groundwater solutes, followed by batch reactivity assessment using TCE as the probe contaminant. A series of sulfidation treatments for ZVI were conducted with an aim to select the treatment parameters that produce the highest material yield, TCE reaction rate, and particle stability in air or aqueous environments. Throughout these investigations, a combination of surface and material chemistry characterization techniques were applied to assist in the understanding of the nature of the unmodified, catalyzed, deactivated, and sulfur-treated iron, so that pertinent properties controlling iron reactivity can be identified.

RESULTS AND DISCUSSION

TCE hydrodechlorination with Pd-Fe bimetallic nanoparticles (BMP) was severely impaired by exposure to clean water and chloride ions, whereas Ni-Fe BMPs were strongly susceptible to sulfate and phosphate-induced deactivation. These results suggest that the aqueous stability of Ni-Fe and its deactivating mechanisms are markedly different from those of Pd-Fe BMPs, thus the two types of bimetallic nanoscale iron may require different tactics to mitigate catalyst deactivation and to prolong their functional lives in the groundwater environment.

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An alternative strategy to circumvent particle deactivation is to chemically modify the surface of iron with appropriate sulfur precursors under controlled conditions to create a series of surface-sulfided iron (SSZVI). Figure 1(a) shows the degradation of TCE in the presence of unaltered nanoscale ZVI (denoted as nanoFe) and those treated with a dilute thiosulfate solution after particles synthesis via the borohydride reduction method. Rapid decreases in TCE concentrations were noted and product analysis indicated that TCE was primarily converted to ethene along with small amounts of acetylene and ethane. Chlorinated intermediates, such as dichloroethene isomers and vinyl chloride were not identified.

The surface sulfidation treatment was found to be applicable to both laboratory synthesized nanoscale iron and commercial ZVI products. As an example, Figure 1(b) compares the reaction rates of as-received Peerless^{TM} iron powder (PMP 50D) with those that underwent dilute acid washing in 0.1 N HCl and two different sulfidation treatment procedures. Treatments A and B differ by the precursor of sulfur used and whether an acid pre-washing step was performed prior to sulfidation. Both treatments brought about remarkable increases in reaction rates. Furthermore, the sulfided iron was able to sustain its reactivity upon prolonged exposure (up to 6 month) to air or aqueous environment, indicating superior material stability relative to its bimetallic counterparts.

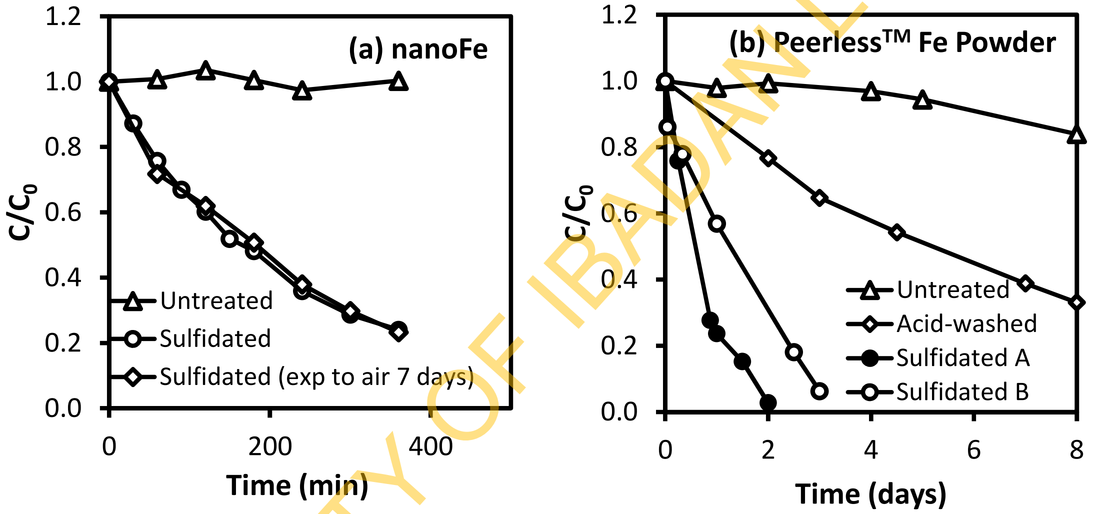

Fig. 1. Effect of surface sulfidation treatment on the reactivity of (a) nanoscale iron and (b) Peerless^{TM} iron power.

CONCLUSIONS

Despite of its enhanced reactivity, bimetallic iron undergoes severe and rapid deactivation in the presence of common groundwater solutes. Furthermore, the catalyst deactivation mechanisms are considerably different for the Ni and Pd-amended BMPs. Compared to the conventional or bimetallic ZVI materials, surface sulfided iron may represent a more robust, effective, and sustainable version of iron for environmental restoration.

REFERENCES

Yan, W. L.; Herzing, A. A.; Li, X. Q.; Kiely, C. J.; Zhang, W. X., Structural Evolution of Pd-Doped Nanoscale Zero-Valent Iron (nZVI) in Aqueous Media and Implications for Particle Aging and Reactivity. *Environmental Science & Technology* **2010,** *44* (11), 4288-4294.

Han, Y.; Yan, W., Bimetallic Nickel-Iron Nanoparticles for Groundwater Decontamination: Effect of Groundwater Constituents on Surface Deactivation. *Water Research* **2014**, *under review*.

Turcio-Ortega, D.; Fan, D.; Tratnyek, P. G.; Kim, E.-J.; Chang, Y.-S., Reactivity of Fe/FeS Nanoparticles: Electrolyte Composition Effects on Corrosion Electrochemistry. *Environmental Science & Technology* **2012,** *46* (22), 12484-12492.

EVALUATING THE MOBILITY OF POLYMER-STABILISED ZERO-VALENT IRON NANOPARTICLES (NZVI)

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INTRODUCTION

One of the main analytical challenges in characterising nanomaterials is related to the difficulty of quantifying them once they are dispersed in complex environmental matrices. Finding new analytical methods to overcome this issue would significantly help in the development of effective remediation materials. In this study, we developed a novel method based on radiolabelling; which enables the detection and quantification of nZVI in intact soil cores.

MATERIALS AND METHODS

Nanomaterials and Soils

Carboxymethyl cellulose (CMC)-nZVI was synthesised according to the methods described by Cirtiu et al. (2011). The isotopic labelling was done during the first stage of the synthesis by spiking $^{59}FeCl_3$ solution into $FeSO_4.7H_2O$ solution.
South Australian topsoil was collected for this study and consists of an uncontaminated sand-loamy soil from Mount Compass (MC) (3 intact soil cores were extracted onsite).

RESULTS AND DISCUSSION

The mobility of radiolabelled CMC-nZVI was assessed in MC soil columns. After an initial leaching period of 72 hours, the columns were left to dry for one month. The irrigation system was then started again for 72 hours to assess the effect of drying/wetting cycle on the mobility of nZVI. Results are presented in Figure 1.
Experimental breakthrough of CMC-nZVI (Figure 1b-d) indicated limited mobility of the nanomaterials in the MC soil columns (i.e. the eluted mass of nZVI was less than 0.0004 of the initial injected mass throughout the experiment). In replicate columns 2 and 3, however, some of the nanomaterials eluted very quickly, within a few minutes after the injection (i.e. $m/m_0 > 0.001$ – Figure 1c and 1d), which is most likely related to preferential flow down the edges of the columns.

After completion of the mobility study, all three columns were dissected into 10 layers (of 1 to 2.5 cm) in order to determine the distribution of retained particles in the columns. The retention profiles of ^{59}Fe-CMC-nZVI in MC soil columns can be found in Figure 2.
Results indicate that about 40 to 65% of the retained particles remained in the first few centimetres; which is most probably related to the rapid aggregation of the nZVI after their injection. The retention profiles of ^{59}Fe-CMC-nZVI in all three columns exhibit a hyperexponential shape with higher retention in the layers next to the column inlet and rapidly decreasing retention with depth.

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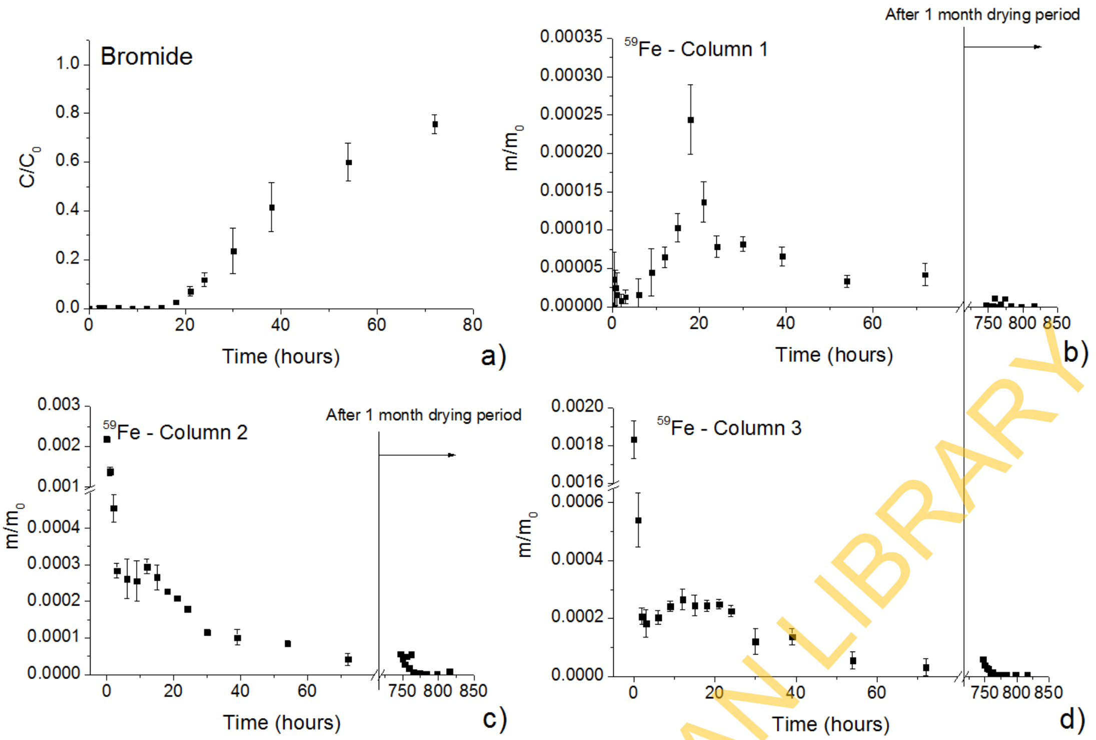

Fig. 1. Summary results of ^{59}Fe-CMC-nZVI mobility in MC soil columns; (a) Experimental breakthrough curve of KBr; (b-d) Experimental breakthrough curve of ^{59}Fe-CMC-nZVI in replicate columns.

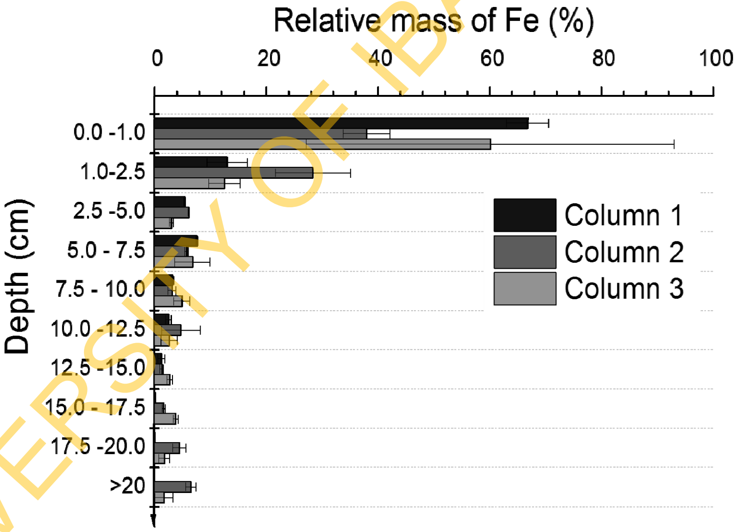

Fig. 2. Retention profiles of ^{59}Fe-CMC-nZVI in MC soil columns. The relative mass of Fe is the mass of Fe per layer divided by the sum of the mass in each layer.

CONCLUSIONS

Compared to previous studies carried out in idealised systems, the results of the present study showed very little translocation of nZVI in intact soil cores. The retention profiles of retained particles showed that most of the particles remained in the first top layers demonstrating the limited effectiveness of this technology.

REFERENCES

Cirtiu C. M., Raychoudhury T., Ghoshal S. and Moores A. 2011 Systematic comparison of the size, surface characteristics and colloidal stability of zero valent iron nanoparticles pre- and post-grafted with common polymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **390** (1-3), 95-104.

DEGRADATION OF MALATHION BY BI-METALLIC Fe-Ni NANOPARTICLES GRAFTED ON PALYGORSKITE

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INTRODUCTION

Malathion (diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate) is an organophosphate para-sympathomimetic pesticide which is extensively used throughout the world to control arthropod pests in public health programs, animal ecto-parasites, human lice, household insects and to protect stored grains (El-Bini Dhouib et al. In press). The key mechanism of malathion and other organophosphates for killing pests is to bind irreversibly to acetylchlinesterase (AChE), which induces an accumulation of acetylcholine and acute neurotoxicity (Noradoun et al. 2005). Similarly, malaoxon (diethyl 2-(dimethoxyphosphorylsulfanyl)butanedioate) is an oxygen derivative of malathion which can either be found as an impurity of malathion or generated during its oxidation in the air or soil (Noradoun et al. 2005). Malaoxon has a much higher binding efficiency to AChE and therefore poses a higher toxicity. It is considered similar to organophosphours nerve agents such as VX (Noradoun et al, 2005).

Detoxification or separation of organophosphorus contaminants without leaving any toxic by-product is necessary. They could be degraded into non-toxic low molecular weight acids by nano zero valent iron (nZVI) with the addition of ethylenediaminetetraacetic acid (EDTA) in a Fenton like reaction (Noradoun et al, 2005). However, nZVI pose disadvantages such as instantaneous agglomeration, passivation in catalytic activity over time, and energy intensive recovery of the nanoparticles following contaminant treatment. These drawbacks could be overcome by using bi-metallic nanoparticles and/or grafting the nanoparticles on clay minerals (Xi et al. 2011).

In this study, we aim to disperse and graft bi-metallic nanoparticles (Fe with Ni) on to bentonite clay in order to convert malathion and malaoxon to non-toxic products by means of activated oxygen generated in the metal-EDTA reactions.

METHODS

Bi-metallic (Fe:Ni = 3:1) nanoparticles were grafted on an acid treated (0.5M HCl at 60°C for 24 h) Australian bentonite (clay:metal = 2:1). Mixed-metal solution was added gradually to well-suspended bentonite in 1M sodium borohydride under N_2 atmosphere. The product was separated by centrifugation, washed with 3:1 ethanol-water mixture, and dried for 12 h at 40°C. The bi-metallic nanoparticles grafted on bentonite (NP-bentonite) was characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy techniques.

Malathion (0.15 mM) degradation experiment was conducted in 0.15 mM EDTA by adding 0.2 g of NP-bentonite at pH value adjusted to 6 by adding concentrated H_2SO_4. The reaction mixture was stirred magnetically for 20 h. Then the suspension was filtered through a 0.2 µm syringe filter and the filtrate was extracted with a solvent mixture (hexane-ethyl acetate; 50:50 v/v). The concentrations of malathion and malaoxon were then determined by a Gas Chromatography – Mass Spectrometer (GC-MS).

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RESULTS AND DISCUSSION

Material characteristics

XRD investigation indicated insertion of some bi-metallic nanoparticles in the inter-layer space of bentonite. No significant Fe or Ni reflection was observed. The absence of strong metal reflections may be due to the small mass percentage of metals present in the product and/or due to the poor crystallinity of metal phases (Xi et al. 2011). SEM images showed an even dispersion of the nanoparticles on the clay surface. A fast XPS scan showed 0.61% Fe and 0.12% Ni in the NP-bentonite. Based on the principle that the number of photoelectron of a certain element is dependent on the atomic concentration of that element in the sample, the relative chemical composition (e.g., oxidation states of metals) was quantified by using the peak areas obtained in high resolution XPS spectra. Zero valent Ni was found in the sample, while Fe existed mostly in di-valent form as oxides.

Malathion degradation

The results showed 100% degradation of malathion (below GC-MS detection limit) from a 0.15 mM initial concentration by 0.2 g NP-bentonite in 20 h (Fig. 2). This removal efficiency was similar to that of the NP-EDTA system alone in the absence of bentonite. The final pH value of the reaction mixture after 20 h was recorded as 5.1. The metabolites of the degradation process were identified (by using the GC-MS library) as butanedioic acid diethyl ester, carbon dioxide and water. No malaoxon was found at the end of the degradation reaction.

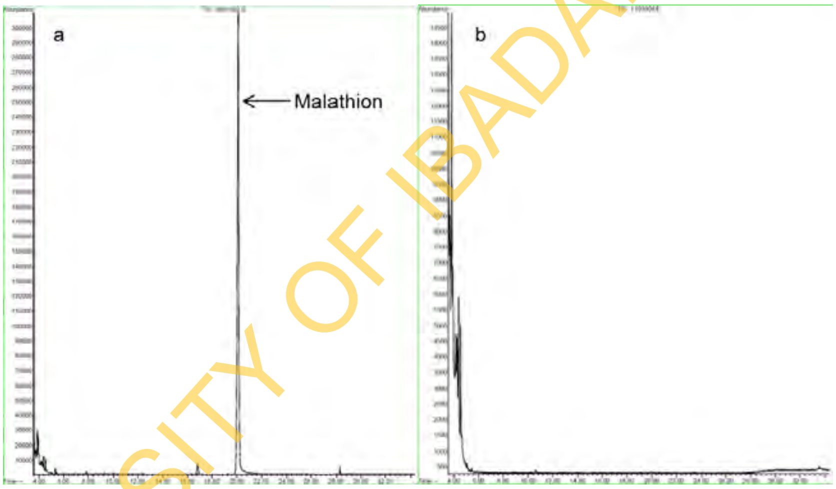

Fig. 2. Chromatogram (a) before, and (b) after treating malathion with NP-bentonite and EDTA.

CONCLUSIONS

This study demonstrated successful grafting of Fe-Ni nanoparticles on bentonite clay, which could degrade malathion without leaving any harmful by-product. In the presence of EDTA, the NP-bentonite produced reactive oxygen species necessary to degrade malathion.

REFERENCES

El-Bini Dhouib, I., Lasram, M.M., Annabi, A., Gharbi, N. and El-Fazaa, S. (In press) A comparative study on toxicity induced by carbosulfan and malathion in Wistar rat liver and spleen. *Pestic. Biochem. Physiol.* (In press), doi:10.1016/j.pestbp.2015.03.012.

Noradoun, C.E., Mekmaysy, C.S., Hutcheson, R.M. and Cheng, I.F. (2005) Detoxification of malathion a chemical warfare agent analog using oxygen activation at room temperature and pressure. *Green Chem.* 7: 426-430.

Xi, Y., Megharaj, M. and Naidu, R. (2011) Dispersion of zerovalent iron nanoparticles onto bentonites and use of these catalysts for orange II decolourisation. *Appl. Clay Sci.* 53: 716-722.

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1D and 3D MnO_2 FOR CATALYTIC OXIDATION OF ORGANIC POLLUTANTS

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INTRODUCTION

Recently, sulfate radicals generated from peroxymonosulfate (Oxone®, PMS) or persulfate (PS) have been applied as an alternative to hydroxyl radicals. Neither homogeneous Co^{2+}/PMS nor heterogeneous catalysis utilizing supported cobalt oxides can completely avoid the leaching or loss of cobalt ions, thus resulting in secondary metal pollution.(Liang et al., 2012) Manganese oxides are abundant in soils and have various forms such as MnO, MnO_2, Mn_2O_3 and Mn_3O_4. Due to variation of the oxidation states between 2+ and 4+ redox cycles, manganese oxides have excellent oxygen mobility in the oxide lattices and thus induce superior redox reactions. In this study, 1D and 3D shape-controlled manganese oxides were prepared and employed to activate peroxymonosulfate to produce sulfate radicals for catalytic oxidation of organic pollutants. The mechanism was also discussed.

METHODS

Synthesis of 1D Manganese oxides

MnO_2 nanorods and nanotubes were prepared by a hydrothermal route using $KMnO_4$ and HCl at 120 and 140 ^oC, respectively. The obtained samples were labelled as Mn-nanorods and Mn-nanotubes, respectively. MnO_2 nanowires were synthesized using manganese sulfate hydrate and potassium permanganate at 140 ^oC for 12 h. The product was referred as Mn-nanowires.(Wang, Indrawirawan, et al., 2015)

Synthesis of 3D Manganese oxides

3 D-hierarchically structured MnO_2 was prepared by a modified hydrothermal process with reduction of $KMnO_4$ with HCl at 60, 100 and 110 ^oC for 12 h, respectively. Referring to the hydrothermal temperature, the obtained samples were labelled as Mn-60, -100 and -110, respectively.(Wang, Sun, Ang, Tade, & Wang, 2015)

Characterization of Samples

X-ray diffraction (XRD) patterns, sscanning electron microscopy (SEM), N_2 adsorption/desorption were used to investigate the properties of the samples.

Catalytic oxidation of phenol solutions

Phenol degradation tests were carried out in a glass reactor containing 500 mL phenol solutions. The reactor was attached to a stand and dipped into a water bath with a temperature controller. Unless specifically stated, reaction temperature was 25 ^oC and phenol initial concentration was 20 ppm. The concentrations of phenol and intermediates were analyzed using a Varian HPLC with a UV detector set at $\lambda = 270$ nm.

RESULTS AND DISCUSSION

Fig. 1(A) shows the adsorption and degradation profiles of phenol over three 1D α-MnO_2 nanomaterials. Control experiments were first carried out to reveal phenol removals induced by adsorption and PMS self-oxidation. Negligible phenol degradation occurred when PMS alone was used. A decline of less than 5% in phenol concentration was found after 90 min without a catalyst. For the adsorption tests, similar phenol removal profiles were observed for the three 1D catalysts in which phenol removal fluctuated in the first 30 minutes to achieve adsorption/desorption equilibrium. For catalytic reactions with PMS, it was shown that commercial activated MnO_2 could not effectively activate PMS for phenol degradation and 80% of phenol was still remained after 90 min. All the 1 D α-MnO_2 can effectively activate

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PMS to achieve fast phenol degradation. As seen, α-MnO_2 nanowires demonstrated the highest phenol degradation rate and thus indicated the best catalytic activity. It removed 100% phenol within 30 min. α-MnO_2 nanotubes possessed the lowest catalytic activity but phenol was fully degraded in 60 min. Fig. 1(B) 4 presents phenol removal profiles under various reaction conditions. For catalytic reactions with the presence of PMS, all the three 3D MnO_2 nanostructures demonstrated superior catalytic activity to the commercial activated MnO_2 which provided a less than 20% phenol degradation after 120 min. Corolla-like Mn-100 showed the highest activity for activation of PMS to produce sulfate radicals and 100% phenol removal was achieved within 30 min. Sea-urchin like MnO_2 (Mn-110) possessed a lower activity and provided 100% phenol removal in 45 min. While Mn-60 presented the least phenol degradation rate and 100% phenol removal was achieved after 60 min.

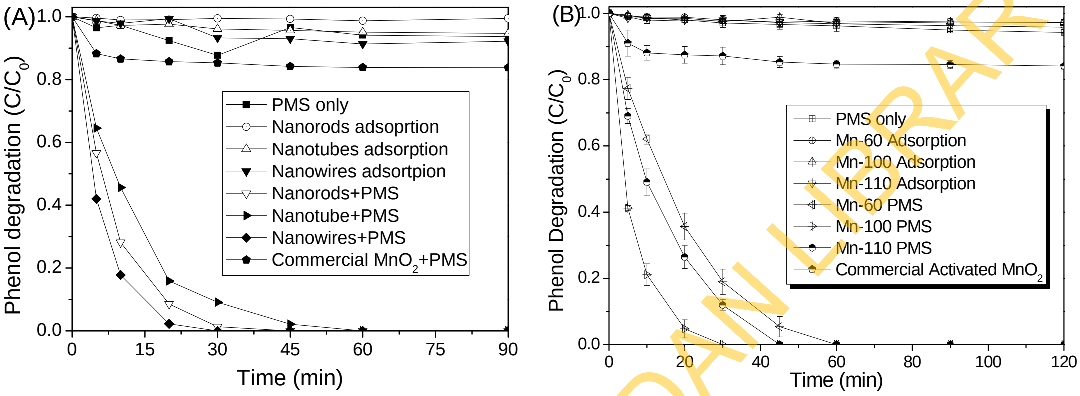

Fig. 1. Catalytic oxidation of phenol solutions with sulfate radicals on (A) 1D MnO_2, and (B) 3D MnO_2 materials

The mechanism of PMS activation and the roles of reactive radicals were investigated by electron paramagnetic resonance (EPR) spectra and competitive radical tests. It was found that the sulfate radicals were the major reactive species responsible for the phenol oxidation.

CONCLUSIONS

Several 1D α-MnO_2 catalysts with shapes of nanorods, nanotubes and nanowires were prepared by a one-step hydrothermal method. α-MnO_2 nanowires showed the highest BET surface area and largest amount of hydroxyl radical generation thus presenting the best catalytic activity. Shape-controlled 3D MnO_2 hierarchical nanostructures were fabricated via a facile one-step hydrothermal method. Corolla-like δ-MnO_2, prepared at a hydrothermal temperature of 100 ^{o}C, showed 2D compact layers of nanosheets on the surface. The mechanism of catalytic reaction for PMS activation was investigated by EPR spectra and showed that both of $^{\bullet}OH$ and $SO_4^{-\bullet}$ are produced in the activation processes, and $SO_4^{-\bullet}$ plays a more critical role in phenol oxidation.

REFERENCES

Liang, H. W., Sun, H. Q., Patel, A., Shukla, P., Zhu, Z. H., & Wang, S. B. (2012). Excellent performance of mesoporous Co_3O_4/MnO_2 nanoparticles in heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions. *Appl. Catal., B, 127*, 330-335.

Wang, Y. X., Indrawirawan, S., Duan, X. G., Sun, H. Q., Ang, H. M., Tade, M. O., & Wang, S. B. (2015). New insights into heterogeneous generation and evolution processes of sulfate radicals for phenol degradation over one-dimensional alpha-MnO_2 nanostructures. *Chem. Engin. J., 266*, 12-20.

Wang, Y. X., Sun, H. Q., Ang, H. M., Tade, M. O., & Wang, S. B. (2015). 3D-hierarchically structured MnO_2 for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: Structure dependence and mechanism. *Appl. Catal., B, 164*, 159-167.

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REMOVAL OF 2,4-DICHLOROPHENOL BY STABILIZED NANO-SCALE ZERO VALENT IRON

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INTRODUCTION

Nano-scale zero valent iron (nZVI) in-situ remediation technology has been widely studied in the past decades (Shih et al., 2011, Arvaniti et al., 2015). A lot of contaminants can be removed by nZVI, including nitrate, heavy metals, halogenated organics (Yu et al., 2014). However, nZVI has some disadvantages: first, nZVI nanoparticles easily trend to aggregate with each other due to the magnetic force and van der waals force, forming micro-scale or even larger particles; second, the nZVI surface will be covered by the iron (hydr)oxides generated during the reaction, which will overlap the active sites and passivate the nZVI; third, nZVI nanoparticles are difficult to recycle due to the extremely size, and secondary pollution may be produced. These defects will restrict the nZVI application for the remediation of contaminated sites.

Some special materials have been used to stabilize the nZVI nanoparticles and inhibit the aggregation and passivation, such as activated carbon, organobentonite, resin, and carboxymethylcellulose (He and Zhao, 2007, Chang et al., 2011). Magnetic composites, polyacrylamide modification and other preparation methods have applied to enhance the separation of nZVI from aqueous phase (Wang et al., 2015).

In our study, an environmentally friendly and novel material, multi-walled carbon nanotubes (MWCNTs) was used to support the palladium-doped nZVI (Pd/Fe) nanoparticles and adsorb 2,4-dichlorophenol (2,4-DCP). In addition, nano-scale Fe_3O_4 was introduced to stabilize Pd/Fe nanoparticles and improve the retrievability via a magnetic separation.

METHODS

MWCNTs-supported Pd/Fe (Pd/Fe@MWCNTs), Fe_3O_4-stablized Pd/Fe (Pd/Fe@Fe_3O_4), and MWCNTs-Fe_3O_4-Pd/Fe (Pd/Fe-Fe_3O_4@MWCNTs) nanocomposites were prepared in a 1000mL three-necked flask under stirring (500 rpm) and nitrogen atmosphere (30 ºC), respectively. The detail preparations were shown as following:

$$\begin{gathered} MWCNTs + FeSO_4 \xrightarrow[20\ \text{min}]{ultrasonic} Fe^{2+} @ MWCNTs \xrightarrow[dropwise]{NaBH_4} \\ Fe^0 @ MWCNTs \xrightarrow[3\,times]{wash} \xrightarrow[1\,h]{K_2PdCl_6} Pd/Fe@MWCNTs \end{gathered} \tag{1}$$

$$\begin{gathered} FeCl_3 + FeSO_4 \xrightarrow[20\ \text{min}]{ultrasonic} \xrightarrow[dropwise]{NH_3H_2O} Fe_3O_4 \xrightarrow[3\,times]{wash} \\ \xrightarrow[ultrasonic]{FeSO_4} \xrightarrow[dropwise]{NaBH_4} Fe^0 @ Fe_3O_4 \xrightarrow[1\,h]{K_2PdCl_6} Pd/Fe@Fe_3O_4 \end{gathered} \tag{2}$$

$$\begin{gathered} MWCNTs + FeCl_3 + FeSO_4 \xrightarrow[20\ \text{min}]{ultrasonic} \xrightarrow[dropwise]{NH_3H_2O} Fe_3O_4 @ MWCNTs \xrightarrow[ultrasonic]{FeSO_4} \\ \xrightarrow[dropwise]{NaBH_4} Fe^0 - Fe_3O_4 @ MWCNTs \xrightarrow[1\,h]{K_2PdCl_6} Pd/Fe - Fe_3O_4 @ MWCNTs \end{gathered} \tag{3}$$

Batch experiments of 2,4-DCP removal were performed in the three-necked flask containing freshly prepared nanocomposites under stirring and nitrogen flow. Aqueous samples were periodically collected through 0.45 μm filter membrane and detected by HPLC.

RESULTS AND DISCUSSION

As shown in Fig. 1, the 2,4-DCP removal was greatly improved after the stabilization of Pd/Fe by MWCNTs. Simultaneous adsorption and dechlorination of 2,4-DCP was observed in Pd/Fe@MWCNTs and Pd/Fe-Fe_3O_4@MWCNTs system. 2,4-DCP was rapidly adsorbed by MWCNTs and gradually dechlorinated. The intermediate products maintained at a very low concentration, and most of the final product was released to liquid phase due to lower adsorption capacity. Moreover, the 2,4-DCP dechlorination was obviously enhanced via the introduction of Fe_3O_4, which would attract the iron (hydr)oxides and inhibit the passivation. Magnetic separation method was proposed to conveniently retrieve the nanocomposites after reaction.

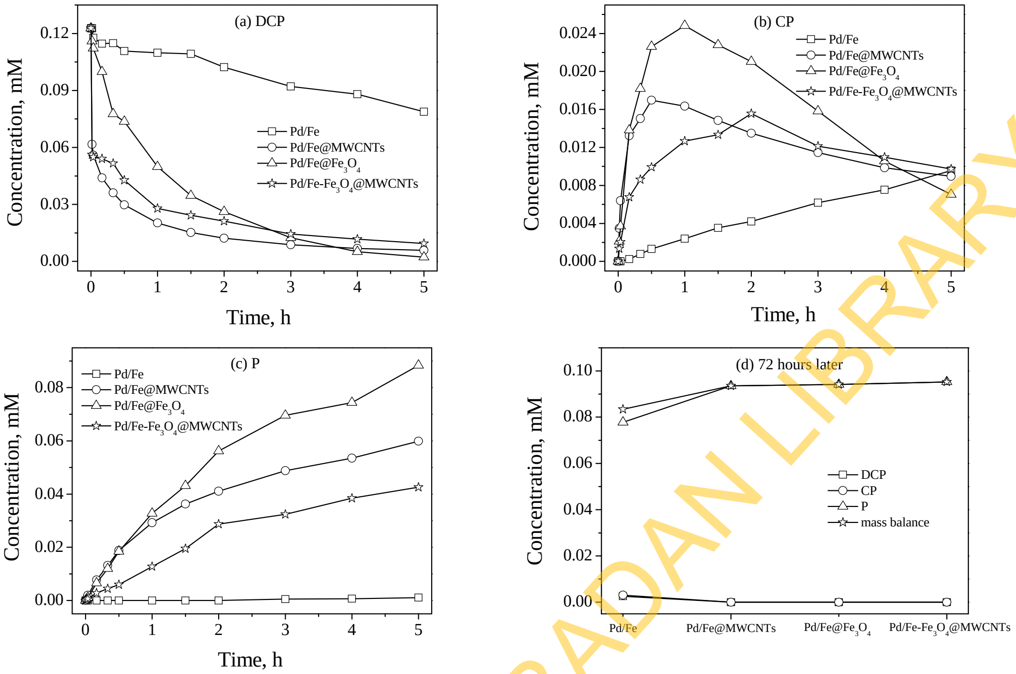

Fig. 1. **Removal of 2,4-DCP by bare Pd/Fe, Pd/Fe@MWCNTs, Pd/Fe@Fe_3O_4, and Pd/Fe-Fe_3O_4@MWCNTs nanocomposites (T=30 ºC, pH=6.0, 3 g L^{-1} nZVI with 0.20 wt% Pd loading, 3 g L^{-1} MWCNTs, 2 g L^{-1} Fe_3O_4).**

CONCLUSIONS

Pd/Fe@MWCNTs, Pd/Fe@Fe_3O_4, and Pd/Fe-Fe_3O_4@MWCNTs showed stronger activity than bare Pd/Fe, suggesting the excellent combination of Pd/Fe with MWCNTs and Fe_3O_4. Pd/Fe-Fe_3O_4@MWCNTs would inhibit the aggregation and passivation of nZVI, and provide a simple way to retrieve the nanocomposites via an extra magnetic field.

REFERENCES:

Arvaniti, O.S., Hwang, Y., Andersen, H.R., Stasinakis, A.S., Thomaidis, N.S. and Aloupi, M. (2015) Reductive degradation of perfluorinated compounds in water using Mg-aminoclay coated nanoscale zero valent iron. *Chem. Eng. J.* 262:133-139.

Chang, C., Lian, F. and Zhu, L. (2011) Simultaneous adsorption and degradation of γ-HCH by nZVI/Cu bimetallic nanoparticles with activated carbon support. *Environ. Pollut.* 159:2507-2514.

He, F. and Zhao, D. (2007) Manipulating the Size and Dispersibility of Zerovalent Iron Nanoparticles by Use of Carboxymethyl Cellulose Stabilizers. *Environ. Sci. Technol.* 41:6216-6221.

Shih, Y., Chen, M. and Su, Y. (2011) Pentachlorophenol reduction by Pd/Fe bimetallic nanoparticles: Effects of copper, nickel, and ferric cations. *Appl. Catal. B: Environ.* 105:24-29.

Wang, W., Li, S., Lei, H., Pan, B. and Zhang, W. (2015) Enhanced separation of nanoscale zero-valent iron (nZVI) using polyacrylamide: Performance, characterization and implication. *Chem. Eng. J.* 260:616-622.

Yu, R., Chi, F., Cheng, W. and Chang, J. (2014) Application of pH, ORP, and DO monitoring to evaluate chromium(VI) removal from wastewater by the nanoscale zero-valent iron (nZVI) process. *Chem. Eng. J.* 255:568-576.

IMPLICATIONS OF MICROBIAL CARBON USE EFFICIENCY IN CONTANMINATED SOIL

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INTRODUCTION

Soil is the largest terrestrial carbon (C) sink, containing approximately 4000 Pg C (Lal, 2013). Microorganisms are at the core of below ground detrital carbon (im)mobilization process. Microbial decomposition contributes significantly to soil respiration as well as soil C transformation and immobilization (Farrell et al., 2011). The conversion of the detrital SOM to newly formed microbial biomass C, defined as carbon use efficiency (CUE), is an indicator of net carbon sequestration and soil quality. Heavy metal inputs from waste disposal and mining activities have become a major source of soil contamination (Bolan et al., 2014). Toxicity of heavy metals may cause a significant impact on microbial activity, and consequently affect carbon dynamics as well as microbial CUE. Produced by pyrolysis process, C content in biochar is highly (poly)aromatic and recalcitrant. Heavy metals may bind with biochar due to the (poly)aromatic structure and, in most cases, negative charges on its surface. Biochar applied to soil may simultaneously increase C sink and also improve soil health. The objective of this study was to evaluate the effect of heavy metal toxicity on microbial CUE and the mechanisms of soil remediation by biochar.

METHODS

Uncontaminated soil and heavy metal (Cd, Cu and Zn at 2.4, 97.5 and 188 mg kg^{-1}, respectively) contaminated soil samples were used in this study. Soil amended with macadamia nutshell biochar (24.3 t ha^{-1}) were also used to examine its effect on the bioavailability of heavy metals. Microbial biomass carbon, microbial respiration and CUE will be measured in these soils.

Two approaches were used to measure microbial CUE:
(i) based on MBC increase,

$$CUE_{mic} = \Delta MBC/(\Delta MBC + \Sigma CO_2\text{-}C) \quad (1)$$

(ii) based on carbon substrate depletion,

$$CUE_{sub} = (\Delta SC - \Sigma CO_2\text{-}C)/\Delta SC \quad (2)$$

where, CUE_{mic} and CUE_{sub} are CUE measured by microbial cumulating and substrate depletion, separately; ΔSC is the depletion of total organic C concentration; ΣCO_2-C is the CO_2 cumulative microbial respiration; ΔMBC is the change in microbial biomass carbon.

The fumigation-extraction method was used to measure microbial biomass carbon (MBC) (Vance et al., 1987). Substrate depletion was measured as the decrease of soil total organic C by a combustion method using a Leco CN analyser (Leco TruMac® CNS). Microbial activity was determined by monitoring the release of CO_2 in 24 hours incubation, which was measured using titration of NaOH with 0.03 M HCL (Bloem et al., 2005).

RESULTS AND DISCUSSION

Table 1. Microbial carbon use efficiency in uncontaminated and contaminated soil samples

CUE approaches	Microbial CUE		
	Uncontaminated soil	Contaminated soil	Biochar amended contaminated soil
CUE_{mic}	0.802	0.542	0.619
CUE_{sub}	0.480	0.322	0.437

In general, CUE_{mic} is higher than CUE_{sub} (Table 1). The higher CUE_{mic} value indicates a higher microbial biomass production with less CO_2-C production. Microbial CUE values for three soil samples followed: uncontaminated > biochar amended contaminated > contaminated. Heavy metal contamination has been shown to decrease both microbial activity as well as MBC production. Microbial CUE depends on the C (im)mobilization rate as affected by soil pollution. The soil samples used in this study were sandy (89.05%, clay 1.97%) and had a low pH (3.72) (Khan, 2015). Nwuche and Ugoji (2008) reported that heavy metal toxicity can be highly pH dependent and acid soils may enhance the bioavailability of heavy metals by increasing their solubility. The biochar type used in this are highly alkaline (pH 10.29). Therefore, the increase of soil pH in biochar amended soil may be attributed to an improvement of microbial activity, therefore a higher CUE. Specific- and non-specific adsorption of heavy metals by soil organic matter (OM) might have occurred because of biochar-induced pH increase, thereby leading to lowering of metals in soil porosity water and consequently microbial CUE increase. In conclusion, the large surface area, porous structure and nutrients content of biochar might also have a positive effect on microbial CUE.

CONCLUSIONS

Microbial CUE in soil varies depending on the approach used to measure CUE. Heavy metal contamination decreased both MBC and microbial respiration, thereby decreasing microbial CUE. The increase in microbial CUE in biochar amended soil may be attributed to the decrease in the bioavailability of heavy metals thereby mitigating microbial toxicity.

REFERENCES

BLOEM, J., HOPKINS, D. W. & BENEDETTI, A. 2005. *Microbiological methods for assessing soil quality*, CABI.

FARRELL, M., HILL, P. W., WANNIARACHCHI, S. D., FARRAR, J., BARDGETT, R. D. & JONES, D. L. 2011. Rapid peptide metabolism: A major component of soil nitrogen cycling? *Global Biogeochemical Cycles,* 25.

KHAN, N. 2015. *Synthesis of biochar amended composts and their evaluation for bioremediation of a sandy soil contaminated with trace metals cadmium, copper and zinc.* PhD thesis, University of South Australia, Australia.

LAL, R. 2013. Climate-resilient agriculture and soil organic carbon. *Indian J. Agron.,* 58**,** 440-450.

NWUCHE, C. O. & UGOJI, E. O. 2008. Effects of heavy metal pollution on the soil microbial activity. *International Journal of Environmental Science & Technology,* 5**,** 409-414.

VANCE, E. D., BROOKES, P. C. & JENKINSON, D. S. 1987. An extraction method for measuring soil microbial biomass C. *Soil Biology and Biochemistry,* 19**,** 703-707.

THE APPLICATION OF NANOPARTICLE MODIFIED ELECTRODES IN MICROBIAL FUEL CELLS FOR ELECTRICITY GENERATION

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INTRODUCTION

Microbial fuel cell (MFC) is the most extensively descried bio-electrochemical systems (BESs) attribute to its ability in recovering energy from low-value biomasses such as wastewaters and purifying wastewater at the same time. It provides a prospective way for sustainable industrial and environmental biotechnological processes(Logan and Regan 2006). The performance of electrodes are the most important aspects in improving the power density and the application of MFCs in large scale. Surface modification of electrode is a hot topic in the research field of MFCs since surface treatments and electroactive coatings can increase surface area and enhance electron collection of the electrode (Wei et al. 2011). Recent advances in nanofabrication provide a unique opportunity to develop efficient electrode materials due to the remarkable structural, electrical, and chemical properties of nanomaterials. Therefore, we aim to design an easy, low-cost and eco-friendly synthesis process of nanomaterials for the modification of the electrode, eliminating the generation of hazardous substances while enhancing the productivity of MFC.

METHODS

In this research, we constructed MFC systems with mixed cultures to achieve substantially greater power densities. A typical group of microorganisms were selected from contaminant position to set up the MFC systems. Nano-particles were synthesized in situ on the carbon based electrodes using green synthesis methods. The modified electrodes were characterized with electron microscopy, including scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as well as various electrochemical methods.

RESULTS AND DISCUSSION

First, to maintain the stability of the BESs used in the deposit of pollutions, the group of microorganisms used as biocatalyst should be carefully selected according to the usage of the BESs. It is reported that a mixed group of microorganisms from aerobic sludge, anaerobic sludge and wetland sediment degrade 92% COD from confectionary wastewater(Sun et al. 2009). And the algae can be used as nutrient source for the microbes present in activated sludge then enhance electricity generation in microbial fuel cell(Rashid et al. 2013). However, researches on BESs development using recalcitrant contaminants as fuels are so few and the possibility and the efficiency are still needed for further study. We selected a group of microorganisms for the biodegradation and detoxification of total petroleum hydrocarbons (TPHs) in the remediation of oil contaminated site as well as for the reuse of the renewable energy to produce electricity.

Second, the performance of the electrodes should be modified in order to make them more efficiency and make the electrochemical losses limited to achieve high current densities. Besides, bio-electrodes use electrochemically active microorganisms have been demonstrated to be capable in improve the performance of BESs, but these biocatalysts based on graphite or carbon electrodes have high electrical resistivity which may cause high electrode ohmic losses(Rozendal et al. 2008). The green synthesized nanoparticles could be applied to enhance the efficiency and limit the electrode losses since nanoparticles have extremely small size and large surface to volume ratio that improve catalytic activity(Xie et al. 2014). Besides, green synthesised nanoparticles using eco-friendly and biocompatible reagents is more economical and could lower the toxicity of the resulting materials as well as the environmental impact of by products(Banerjee et al. 2014).

CONCLUSIONS

In conclusion, we constructed MFC systems with a mixed cultures selected from contaminant position to set up the MFC system. Nano-particles were synthesized in situ on carbon based substrate by plant-mediated reduction with high crystallinity and fine dispersion.

REFERENCES

Banerjee, P., Satapathy, M., Mukhopahayay, A. and Das, P. (2014) Leaf extract mediated green synthesis of silver nanoparticles from widely available Indian plants: synthesis, characterization, antimicrobial property and toxicity analysis. Bioresources and Bioprocessing, 1(1), pp. 1-10.

Logan, B. E. and Regan, J. M. (2006) Microbial fuel cells-challenges and applications. Environmental science & technology, 40(17), pp. 5172-5180.

Rashid, N., Cui, Y.-F., Saif Ur Rehman, M. and Han, J.-I. (2013) Enhanced electricity generation by using algae biomass and activated sludge in microbial fuel cell. Science of the Total Environment, 456, pp. 91-94.

Rozendal, R. A., Hamelers, H. V., Rabaey, K., Keller, J. and Buisman, C. J. (2008) Towards practical implementation of bioelectrochemical wastewater treatment. Trends in biotechnology, 26(8), pp. 450-459.

Sun, J., Hu, Y., Bi, Z. and Cao, Y. (2009) Improved performance of air-cathode single-chamber microbial fuel cell for wastewater treatment using microfiltration membranes and multiple sludge inoculation. Journal of Power Sources, 187(2), pp. 471-479.

Wei, J., Liang, P. and Huang, X. (2011) Recent progress in electrodes for microbial fuel cells. Bioresource technology, 102(20), pp. 9335-9344.

Xie, Y., Fang, Z., Qiu, X., Tsang, E. P. and Liang, B. (2014) Comparisons of the reactivity, reusability and stability of four different zero-valent iron-based nanoparticles. Chemosphere, 108, pp. 433-436.

BIOREMEDIATION OF MERCURY BY BACTERIAL STRAINS RECOVERED FROM CONTAMINATED SOIL

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INTRODUCTION

The conventional physicochemical methods of Hg remediation are expensive and create disposal problem of Hg loaded biomass. The key Hg resistance mechanism in Hg resistant bacteria is reduction of toxic Hg^{2+} to Hg^0 which is subsequently volatilized from cell (Summers and Lewis, 1973). The bacterial Hg volatilization character has been utilized in the present study to bio-remediate Hg by bacterial isolates recovered from contaminated soil.

METHODS

The Hg resistant bacteria were isolated from three contaminated soil samples by enrichment technique in an inorganic Hg (as $Hg(NO_3)_2$) supplemented low phosphate (LP) medium. The bacterial isolates were identified by 16s rRNA gene sequencing. Hg resistance (expressed as EC_{50}) of the bacterial isolates were determined in Hg supplemented LP media by measuring their growth as OD_{600}. Hg volatilization ability of bacterial strains was qualitatively detected by a modified photographic film method (Nakamura and Nakahara, 1988). The mercuric reductase gene *merA* in each isolate was detected by PCR and sequenced. NADH dependent Mercuric reductase enzyme activity was determined by spectrophotometric method. Bioremediation of Hg by the isolated strains was primarily tested in solution. Hg-supplemented LP media was inoculated with mid log phase bacterial cultures and Hg depletion was monitored for 12 hours at 6 hours intervals. Hg accumulation in dead cell and live cell pellets was also measured. Cellular Hg accumulation was visualized by ESEM-EDX. Bioremediation of Hg from soil by the bacterial isolate was done in 4 soils using one strain. Three soils were spiked with 100 mg/Kg Hg and aged for 120 days; the other soil was a field contaminated soil. Hg contaminated 10g of soils were taken in 50 ml polypropylene tubes and inoculated with 10% (v/w) mid log phase bacterial culture. The moisture contents of the soils were brought to 70% of total water holding capacity by sterile distilled water and kept constant. Effect of nutrient on bioremediation was tested by adding 1% (w/v) sterile nutrient broth. Controls didn't get any inoculum or nutrient. Hg was measured at 0, 7th, 14th and 28th day. All Hg analyses were done by ICP-QQQ-MS (Agilent Technologies 8800).

RESULTS AND DISCUSSION

Three bacterial strains were isolated from contaminated soils and coded as SA2, SE2 and SE1. 16S rRNA sequences revealed that the isolates have close phylogenetic relation with *Sphingobium* sp. (KJ767657), *Sphingopyxis* sp. (KM603316) and *Pseuodoxanthomonas* sp. (KP843005) respectively. These bacterial genera are reportedly resistance to a number of pollutants including heavy metals (Maeda et al., 2014, Nilgiriwala et al., 2008, Xiao et al., 2011), but there is no report of Hg resistance to our knowledge. The toxicity study in Hg-supplemented LP media revealed that isolate SE2 (*Sphingopyxis*) was highly resistant to inorganic Hg followed by SA2 (*Sphingobium*) and SE1 (*Pseudoxanthomonas*) with estimated 72 hours EC_{50} values 5.97, 4.5, and 1.36 mg/L respectively. Considering the use of less nutritious LP media for resistance test, SA2 and SE1 have the highest Hg resistance compared to other reports. Deduced amino acid sequences of *merA* gene of SA2, SE2 and SE1 (accession KJ866415, KM979432 and KP843006 respectively) showed homology to mercuric reductase enzyme from diverse groups of microorganisms. Mercuric reductase enzyme activities from crude proteins were determined as 35, 24 and 9.7 MU in strain SA2, SE2 and SE1 respectively. All three isolates proved their capability of volatilizing Hg in a modified photographic film experiment. The subsequent bioremediation study revealed that all these isolates could remove Hg from solutions in various degrees. The highest Hg scavenger was strain SA2 that removed almost 80% of initially added mercury (3.2 mg/L) from culture solution in 6 hours. Isolate SE2 and SE1 removed 56% of 3.2 mg/L and 60% of 1.5 mg/L Hg in 6 hours. There was no change in Hg loss for 12 hours. Hg removal occurred only in the live cell containing solutions. There was no decrease in Hg concentrations in dead cell controls as well as abiotic controls. 10-20% Hg was recovered from dead cell pellets. This may be due to sorption of Hg by dead cellular biomass. Live cell pellets accumulated 20 to 40% of Hg. Hg droplets on SA2 cells were detected.

Since the isolate *Sphingobium* SA2 volatilized most of the mercury from solution, it was chosen for Hg remediation from contaminated soil. Four soils of different pH were chosen for the study. In a neutral soil (S-1, pH 7.4) the highest Hg removal (48%) by SA2 was obtained in 14 days without any nutrient. Nutrient and the inoculum together did not change the remediation. Nutrient amendment without the culture showed 38% Hg removal. In alkaline soil (S-2, pH 8.5) the highest 37% removal of Hg obtained in 14 days with the culture alone. Nutrient amendment did not increase the Hg removal in this soil also, but nutrient alone facilitated Hg removal to 33% in 14 days. In an acidic soil (S-3, pH 4.2), Hg removal (37% in 14 days) was mainly due to the inoculum; 13% Hg was removed by nutrient amendment without SA2 culture. Nutrient addition along with the inoculum did not increase remediation in this soil. Conversely in a field contaminated soil (S-4, pH 7), nutrient amendment with the inoculum increased the removal to 65% in 7 days. S-4 is expected to harbour Hg resistant bacterium that could facilitate the removal. In S-4, Nutrient amendment without inoculum increased Hg removal to 50% in 28 days. In control soils of S-1, S-2 and S-3 3 to 5% Hg loss was detected after 28 days; conversely in S-4 this loss was 10%.

CONCLUSION

The isolated bacterial strains are highly Hg resistant which rapidly volatilizes Hg. All of the strains could remove more than half of Hg from solution in 6 hours. One of them (SA2) was tested to remediate Hg contaminated soils. The Hg removal potential of these isolates could be exploited to remediate Hg-contaminated soils and waters in field scale. The volatilized Hg due to remediation can be trapped (yet to be tested) and recovered.

REFERENCES

Maeda, A. H., Nishi, S., Hatada, Y., Ozeki, Y. and Kanaly, R. A. (2014) Biotransformation of the high-molecular weight polycyclic aromatic hydrocarbon (PAH) benzo [k] fluoranthene by *Sphingobium* sp. strain KK22 and identification of new products of non-alternant PAH biodegradation by liquid chromatography electrospray ionization tandem mass spectrometry. *Microbial biotechnology,* 7**:** 114-129.

Nakamura, K. & Nakahara, H. (1988). Simplified X-ray film method for detection of bacterial volatilization of mercury chloride by *Escherichia coli*. *Applied and environmental microbiology,* 54**:** 2871-2873.

Nilgiriwala, K. S., Alahari, A., Rao, A. S. and Apte, S. K. (2008). Cloning and overexpression of alkaline phosphatase PhoK from *Sphingomonas* sp. strain BSAR-1 for bioprecipitation of uranium from alkaline solutions. *Applied and environmental microbiology,* 74**:** 5516-5523.

Summers, A. O. and Lewis, E. (1973). Volatilization of mercuric chloride by mercury-resistant plasmid-bearing strains of *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*. *Journal of bacteriology,* 113**:** 1070-1072.

Xiao, C., Yan, H., Wang, J., Wei, W., Ning, J. and Pan, G. (2011). Microcystin-LR biodegradation by *Sphingopyxis* sp. USTB-05. *Frontiers of Environmental Science & Engineering in China.* 5**:** 526-532.

TWO-WAY INTERACTIONS BETWEEN ORGANOPHOSPHORUS (OP) COMPOUNDS AND SOIL MICROBIAL COMMUNITIES

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INTRODUCTION

Pesticides are applied in agro-ecosystems to reduce the impact of plant pests and pathogens on crop yield in an effort to meet the increased demand for food of Earth's growing population globally. Among the various groups of pesticides applied, organophosphorus (OP) pesticides, e.g. chlorpyrifos (CP), are the most commonly used agrochemicals for its high effectiveness against target pests. The excessive use and lack of appropriate disposal technology has resulted in the contamination of ecosystems globally (Yu *et al*., 2006), impacting the self-regulating capacity of the biosphere. There is also a growing concern of widespread contamination of the environment leading to potential risks to non-target organism, for example soil microbial communities (Omar and Abdel-Sater, 2001).

Assessing the impact of pesticides on soil microbial communities is of importance because they play a vital role in ecosystem services and maintain soil health, which are key requirements for sustainable land use in terms of food security and environmental sustainability (Lo, 2010) . The current work aimed to unravel the two-way interactions between CP and soil microbial communities; i.e., what impacts does CP have on soil microbial functions (*e.g*. biodegradation) and how soil microbial communities modulate CP persistence *via* biodegradation.

METHODS

Two soil treatments (from Australian sugarcane farms) were used in this study; a) one with no history of CP application (1H-5H,non-treated) and b) another with history of CP application (1R-5R, pesticide-treated) about 13 years ago after it was banned in 2002 following the loss of efficacy in Australian sugarcane farm soils. The relationship between CP degradation and soil microbial communities were evaluated in both the soil treatments that were spiked (3 times) with 10 mg/kg of CP under lab conditions. In addition to this, through repetitive enrichment and successive culturing indigenous bacterial strains were examined for their potential to degrade CP and 3,5,6-trichloro-2-pyridinol (TCP, a primary and major CP degradation product) in liquid media under various nutritional conditions.

RESULTS AND DISCUSSION

The results showed that the half-lives of CP decreased with application frequency and were 23-47, 8-20 and 3-17 days following the first, second and third application, respectively (for both soil treatments) particularly the soils from 4R, 4H and 5R that showed enhanced CP degradation even when not exposed to CP for last 13 years due to legacy effect of the pesticide. Furthermore, sequential soil and liquid culture enrichments enabled the isolation of six bacterial CP degraders with sequence homologies to *Xanthomonas* sp. (3), *Pseudomonas* sp. (1), *Rhizobium* sp. (1) and *Lysobacter* sp. (1). The efficacy of the isolated strains: *Xanthomonas* sp. 4R3-M1, *Pseudomonas* sp. 4H1-M3 and *Rhizobium* sp. 4H1-M1 were further investigated for biodegradation of CP and its primary metabolic product, TCP. The results indicated that all three bacterial strains utilised CP (10 mg/l) and TCP (as CP degradation product) in mineral salt media (MSM) as a sole source of carbon (C) and nitrogen (N). Bacterial strains *Xanthomonas* sp. 4R3-M1 and *Pseudomonas* sp. 4H1-M3 could also degrade 10 mg/l TCP as a sole C- and N-source, when provided externally.

CONCLUSIONS

Despite no exposure to CP for 13 years (in fields), this study highlighted that the enhanced degradation capacity of soil microbial community was maintained due to the legacy effect of previous use of the compound. Owing to the widespread use of CP worldwide, this study provide a strong evidence of legacy effects of pesticide on soil microbial communities and the importance of considering long-term management practices in agro-ecosystems. In addition to this, novel CP and TCP degrading bacterial strains were isolated from Australian sugarcane farm soils that showed enhanced degradation of CP in a lab-based study. All strains isolated were able to grow in the presence of CP and/or TCP and were able to degrade CP and/or TCP in a broad range of media with different C, N and phosphorus (P) additions. The use of such efficient indigenous bacterial strains promises to be effective in practical application of bioremediation of both CP and TCP.

REFERENCES

LO, C.-C. 2010. Effect of pesticides on soil microbial community. *Journal of Environmental Science and Health Part B,* 45**,** 348-359.

OMAR, S. & ABDEL-SATER, M. 2001. Microbial populations and enzyme activities in soil treated with pesticides. *Water, Air and Soil Pollution,* 127**,** 49-63.

YU, Y. L., FANG, H., WANG, X., WU, X. M., SHAN, M. & YU, J. Q. 2006. Characterization of a fungal strain capable of degrading chlorpyrifos and its use in detoxification of the insecticide on vegetables. *Biodegradation,* 17**,** 487-494.

EFFECT OF PHOSPHATE ON TOXICITY AND ACCUMULATION OF ARSENIC IN SOIL MICROALGAE

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INTRODUCTION

Arsenic is a toxic metalloid and widely distributed in the environment. The toxicity of arsenic to living organisms not only depends on the concentration but also on the chemical speciation. Between the two predominant inorganic forms of arsenic in aquatic system, arsenite [As(III)] is considered to be more toxic and mobile than arsenate [As(V)] (Neff 1997). However, this statement on the toxic nature of As(III) and As(V) applied mainly to animals and marine phytoplankton, and was reversed in most freshwater microalgae (Karadjova et al. 2008; Wang et al. 2013). Microalgae are an important component of both aquatic and terrestrial ecosystems and potentially could remediate arsenic-contaminated water and soil via biotransformation, bioaccumulation and biosorption. Many freshwater microalgae have been studied for this purpose, however, little is known about soil isolates of microalgae. Being chemically similar to phosphate, As(V) may compete with it in cellular transportation which may affect the toxicity to microalgae as well as cellular accumulation of arsenic. Therefore, we have investigated: (a) the effect of phosphate on the toxic nature of inorganic arsenic species to a soil microalga *Chlorella* sp. in terms of growth inhibition; and (b) the influence of phosphate concentration in the growth medium on bioaccumulation of both As(III) and As(V) in this alga.

METHODS

The axenic culture of microalga *Chlorella* sp. used in this study has been previously isolated from an uncontaminated soil. The toxicity of As(III) as $NaAsO_2$ and As(V) as $Na_2HAsO_4.7H_2O$ to *Chlorella* sp. was determined at three phosphate levels (0.2, 2.0 and 20.0 mg/l) using a 96-h growth inhibition bioassay. Algal cells were added to the sterile culture flasks containing phosphate-amended Bold's Basal Medium (BBM) to reach the final cell density of 10^5 cells/ml. Each test included ten to fifteen arsenic concentrations and a control. The flasks were then placed randomly on an orbital shaker set at 120 rpm and incubated in a temperature-controlled (25°C) room under continuous illumination (200 µE/m^2/s PPED) provided by cool white fluorescent lamps.

To examine the inorganic arsenic bioaccumulation ability, cells were incubated in the BBM amended with two phosphate levels (2 and 20 mg/l). Arsenic was added to the media at a concentration of 75 and 750 µg/l in separate experiments for both As(III) and As(V). The incubation condition was the same as that described above. After 8 d of incubation, the cells were harvested and the total intracellular arsenic content was determined by ICP-MS.

RESULTS AND DISCUSSION

The toxicity test with different concentrations of As(III) and As(V) showed that the As(V) is much more toxic to the present alga irrespective of phosphate concentration in experimental medium (Table 1). This differs from the observation of Levy et al. (2005), where a freshwater *Chlorella* showed almost equal resistance to As(III) and As(V) with the IC50s of 25.2 and 25.4 mg/l respectively. The toxicity of As(V) in our study greatly increased under P-limiting condition. The 96-h IC50s to As(III) were 111.8, 93.8 and 81.2 mg/l in high-, medium- and low- P media respectively. In contrast a 10-fold decrease of phosphate from 20 (high-P) to 2 (medium-P) mg/l increased the toxicity of As(V) to about 15-fold, i.e. IC50 changed from 8.33

to 0.57 mg/l (Table 1). The increased toxicity of As(V) was due to lower phosphate concentrations in the media solution. Due to its chemical similarity to phosphate, As(V) enters the algal cell via phosphate transporters (Wang et al. 2013). Therefore, under low-P condition, the smaller amount of phosphate may not be sufficient to compete with As(V) in the outer cell transporting system.

Table 1 96-h IC50 values of As(III) and As(V) for the *Chlorella* sp. at different initial phosphate concentrations

	96-h IC$_{50}$ (mg/l)	
Initial phosphate level (mg/l)	As(III)	As(V)
0.2	81.2 (61.4–111.8)[a]	0.36 (0.27–0.43)
2.0	93.8 (81.8−106.5)	0.57 (0.51−0.61)
20.0	111.8 (105.5−118.4)	8.33 (6.99−9.24)

[a] Value range in parenthesis indicates 95% confidence limit

Bioaccumulation of arsenic in microalgae has been suggested due to the active uptake mechanism (Maeda et al. 1985). In this study, the alga showed superior bioaccumulation capacity of arsenic when ambient arsenic concentrations increased. However, the initial phosphate concentration in the medium influenced the bioaccumulation capacity. A significant difference ($p<0.05$) was found in the bioaccumulation of arsenic under two phosphate regimes except when the alga was exposed to a lower concentration of As(V), i.e. 75 µg/l. The maximum bioaccumulation of arsenic observed in the phosphate-limiting (2 mg/l) medium containing 750 µg/l As(V) which was 1264 µg/g. Arsenic accumulation capacity was found higher than other microalgae such as *Chlorella vulgaris*, 610 µg/g (Suhendrayatna et al. 1999) and *Scenedesmus* sp., 762 µg/g (Bahar et al. 2013) but less than the *Scenedesmus obliquus* and *Chlamydomonas reinhardtii*, 6331 and 10201 µg/g, respectively (Wang et al. 2013). In view of the high arsenic accumulation capacity, the present alga can be considered as a good arsenic accumulator.

REFERENCES

Bahar, M.M., Megharaj, M. and Naidu, R. (2013) Toxicity, transformation and accumulation of arsenic in a microalga *Scenedesmus* sp. isolated from soil. *J. Appl. Phycol.* 25:913–917.

Karadjova, I.B., Slaveykova, V.I. and Tsalev, D.L. (2008) The biouptake and toxicity of arsenic species on the green microalga *Chlorella salina* in seawater. *Aquat. Toxicol.* 87:264–271.

Levy, J.L., Stauber, J.L., Adams, M.S., Maher, W.A., Kirby, J.K. and Jolley, D.F. (2005) Toxicity, biotransformation, and mode of action of arsenic in two freshwater microalgae (*Chlorella* sp. and *Monoraphidium arcuatum*). *Environ. Toxicol. Chem.* 24:2630–2639.

Maeda, S., Nakashima, S., Takeshita, T. and Higashi, S. (1985) Bioaccumulation of arsenic by freshwater algae and the application to the removal of inorganic from an aqueous phase. Part II. By *Chlorella vulgaris* isolated from arsenic-polluted environment. *Sep. Sci. Technol.* 20:153–161.

Neff, J.M. (1997) Ecotoxicology of arsenic in the marine environment. *Environ. Toxicol. Chem.* 16:917−927.

Suhendrayatna, Ohki, A., Kuroiwa, T. and Maeda, S. (1999) Arsenic compounds in the freshwater green microalga *Chlorella vulgaris* after exposure to arsenite. *Appl. Organomet. Chem.* 13:127–133.

Wang, N.X., Li, Y., Deng, X.H., Miao, A.J., Ji, R. and Yang, L.Y. (2013) Toxicity and bioaccumulation kinetics of arsenate in two freshwater green algae under different phosphate regimes. *Water Res.* 47:2497–2506.

CHALLENGES FOR NATIVE FOREST ESTABLISHMENT ON SURFACE MINES IN A TIME OF CLIMATE CHANGE

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INTRODUCTION

Reclaimed mine soils in the Appalachian coal field of the US often exhibit physicochemical characteristics that are dissimilar to native topsoil. As such, the native forest species that occupied a site prior to mining may not be suitable for establishment under conditions found within the post-mining soil environment. In a time of climate change, native species establishment may be further hindered on these disturbed landscapes. Species distributions are expected to change under current climate models (Prasad et al., 2007). Regardless of which climate change scenario used, pine forests are speculated to be much more responsive to climatic variation than deciduous forests in the eastern US. In the central hardwood region that includes Kentucky; oak distribution is projected to move northward due to climatic change and could be replaced by southern pine species. The consequence of combined land-use disturbance from mining and climate change on native forest establishment is unknown.

Loblolly pine (*Pinus taeda*) is native to the southeastern US, but their current range does not extend as far north as Kentucky. The loblolly pine is relatively fast to mature and has a wide range of uses from pulpwood to plywood to lumber. For these reasons, it is one of the most important commercial timber trees in the US (Burns and Honkala, 1990). The northern red oak *(Quercus rubra*) is a large tree, with a native range that spans from the southeastern US into southeastern Canada and is found throughout Kentucky. Northern red oak is relatively slow to mature, but also an important tree for timber, and can have even higher value as lumber and veneer. Oaks provide around half of the annual production of hardwood lumber in the US (Petrides, 1998). In Kentucky, the economic impact of the timber industry was estimated at $12.8 billion in 2013, of which oak species comprised about one-third of timber sales (Stringer et al. 2014). Even though both species are considered economically important, structurally the trees are greatly different (conifer versus hardwood) and each provides a unique set of ecosystem services specific to their native range. Loss of northern red oak and replacement with loblolly pine will certainly have short-term economic impacts, but potentially long-term effects on wildlife populations und unknown environmental consequences.

METHODS

An experiment to examine the suitability for species replacement due to climate change was initiated in 2004 on a reclaimed coal mine in eastern Kentucky. The project was set up as a factorial experiment with forty-eight 15 x 15 meter plots containing either native northern red oak (NRO) or non-native loblolly pine (LP) (Barton et al., 2008). Half of the plots received an application of 40 tons per acre of a wood chip/manure compost mixture. All plots were subsequently ripped to a depth of approximately 2-meters using a dozer. In each plot, 80 bare-root seedlings of an individual species were transplanted. Survival, diameter and height of trees were measured after the 4th and 10th growing seasons. Diameter and height were used to determine volume growth (cm^3). Herbaceous ground cover was clipped during the 10th growing season within two randomly-placed $1m^2$ sample grids in each plot. Samnples were dried to obtain g/m^2 of herbaceous biomass. During the 11th growing season, soil samples were collected from three locations in each plot to a 10-cm depth and composited. Soils were analyzed for pH, electrical conductivity, carbon and selected nutrients.

RESULTS AND DISCUSSION

Four years after planting, mean survival was 77% for LP and 60% for NRO. Mean growth at Year 4 was 2,532 cm^3 for LP and 62 cm^3 for NRO. After 10 years, dramatic differences in mean growth were observed between LP (199,144 cm^3) and NRO (1,250 cm^3). Year 10 mean survival remained higher for LP (63%) than NRO (38%).

Shade from the closed-canopy LP stand resulted in much lower mean herbaceous cover (39 g/m^2) than that observed on the open-canopy NRO plots (171 g/m^2). Moreover, the rapid growth and shade development in the LP plots provided much more resistance to invasive species colonization than that observed in the NRO plots. Given the low survival of NRO and high levels of competition, future success of these plantings is severely compromised.

Soil pH was similar for both tree types (pH 5.41). Analysis of soil nutrients, however, showed consistently lower values in the LP plots as compared to the NRO plots for all elements examined. Differences are likely due to resource utilization by the faster growing LP stand.

CONCLUSIONS

Results clearly show that conditions on the mined land favor establishment and growth of the non-native LP over that of the native NRO. Although return of the native forest ecosystem is often a reclamation goal, pressure from non-native species could be problematic on disturbed mine lands if climate change species distribution models prove to be accurate. This issue could be exasperated on mined sites over that of an undisturbed forest because the disturbance regime may favor colonization of species that are more adapt to dealing with the combined stress of a new climate and soil environment. A concern that mined sites may be compromised by climate change seems warranted; thus, management practices to deter and prevent species loss and replacement are needed.

REFERENCES

Barton, C.D., Marx, D., Sweigard, R. and Barton, W. (2008) Evaluating Spoil Amendment Use and Mycorrhizal Inoculation on Reforestation Success in the Eastern and Western Kentucky Coalfields. *In*: Proceedings of 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA, New Opportunities to Apply Our Science. R.I. Barnhisel (Ed.) Published by ASMR, Lexington, KY. pp 98-111.

Burns, R. and Honkala, B. (1990) Silvics of North America; Volume 2, Hardwoods. Agricultural Handbook 654. Department of Agriculture, Forest Service, Washington, DC, 877 p.

Petrides, G.A. (1998) A Field Guide to Trees and Shrubs: Northeastern and North-Central United States and Southeastern and South-Central Canada. Boston: Houghton Mifflin.

Prasad, A. M., Iverson, L. R, Matthews, S., and Peters, M. (2007) A Climate Change Atlas for 134 Forest Tree Species of the Eastern United States [database]. http://www.nrs.fs.fed.us/atlas/tree, Northern Research Station, USDA Forest Service, Delaware, Ohio.

Stringer, J., Thompson, B., Ammerman, B. and Davis, A. (2014) Kentucky Forestry Agriculture Impact Report 2013-2014. University of Kentucky, Cooperative Extension Service. FORFS 14-01. http://www2.ca.uky.edu/forestryextension/Economic%20Impact/Economic%20report%202013-2014.pdf

WEB BASED GUIDANCE FOR MINE WASTE REMEDIATION

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INTRODUCTION

The ITRC is a state-led, national coalition of industry, governmental agencies, and stakeholders within the United States dedicated to help interested parties achieve a better understanding of environmental protection through the use of innovative technologies. To achieve its goals, ITRC establishes teams to present guidance on the use of technologies to address major environmental problems facing the states. One of the teams was organized to review various technologies to address mining related environmental issues.

Historical mining practices and the lack of mine land reclamation have led to sites with significant environmental and human health issues. Current ongoing practices have also led to mine waste issues at currently operating sites that must be addressed when operations cease. Typical remedial solutions are often lengthy and expensive, and may be unacceptable to the mining community, the regulatory community and to the public. Some mined sites contain enough residual mineralization that re-mining and subsequent reclamation may be economically feasible. Some current operations may even have the infrastructure in place to co-manage the cleanup of legacy waste while in operation. However, current regulations often provide barriers to these approaches. Innovative approaches and technologies need to be developed and implemented at current and former mining projects that solve our environmental issues and remove existing regulatory barriers. The ITRC Mine Waste team has developed a web-based guidance, ITRC MW-1, 2010 available at http://www.itrcweb.org/miningwaste-guidance/ that helps project managers understand technologies to deal with mine waste.

METHODS

The guidance contains decision trees (see Figure 1), technology overviews, and case studies. The decision trees guide users to a set of treatment technologies that may be applicable to their site and are designed to give the reader options based upon site specific conditions. The decision trees can also be used to identify potential multiple alternatives in cases where specific information is not available to allow the reader to identify potential paths forward. The technology overviews were developed by sub-teams of experts from industry, regulatory agencies, academia, and stakeholders. Each technology overview includes information on applicability, advantages, limitations, performance, stakeholder concerns, regulatory considerations, and lessons learned. Although the technology overviews are not intended or designed to be engineering documents, each contains sufficient information to give the reader a basic understanding of a technology to help the reader determine the potential applicability of the technology to a specific site. The case studies support the technology overviews and give information on documented applications of the various technologies as they were used in actual remedial programs. Where available, the case studies include site-specific information on site history, pre-remedial conditions, project goals, remedial design and construction, stakeholder and regulatory involvement and concerns, and project results. Together, the decision trees, technology reviews, and case help project managers decide how well a technology may fit their remedial/reclamation goals.

RESULTS AND DISCUSSION

The guidance is available, free of charge, to anyone with access to the internet. In addition to the guidance the ITRC Mining Waste Team organized and developed an internet training program to assist interested parties in learning how to use the guidance. Since 2010, over 1,500 individuals participated in the Mining Team training program. The program also identified several remedial areas where there has been a rapid advancement in the state of the science in the last fifteen years. This led to the organization of the Biochemical Reactors for Mining-Influence Water team. The presentation will introduce the guidance and introduce some of the highlights of the technologies presented.

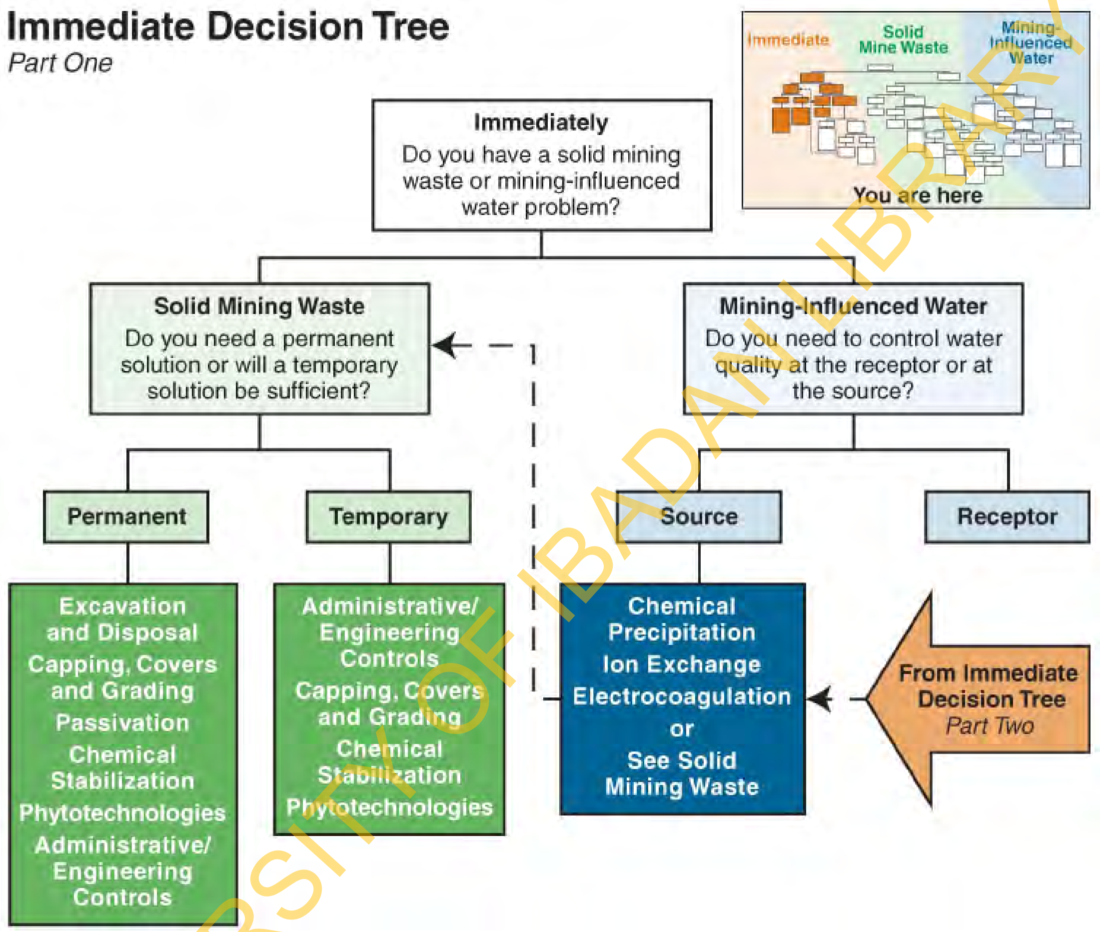

Fig. 1. ITRC Mining Waste Guidance Document Immediate Decision Tree

CONCLUSIONS

Mining is essential to the economy of the United States, but historical mining practices and the absence of routine mined-land reclamation, remediation, and restoration have led to legacy sites with environmental and human health impacts. To help increase acceptance of new technologies for the remediation of mining-related environmental problems, the Interstate Technology Regulatory Council's Mining Waste Team developed a successful web-based program to assist regulators, practitioners, industry, and stakeholders to better understand the available technologies currently in use.

REFERENCES

Mining Waste Treatment Technology Selection, 2010, ITRC Sponsored by Environmental Council of the States, Washington, D.C., Available from: http://www.itrcweb.org/miningwaste-guidance/. [16 July 2015]

MINE SITES — MANAGING THE NEXUS BETWEEN ACTIVE MINE SITES AND CONTAMINATED LAND PHILOSOPHY

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INTRODUCTION

Mining necessarily entails disturbance of the environment. Potential sources of contamination are associated with mining activities including disturbance of the groundwater systems, dewatering of local groundwater, losses from heap leach extraction, tailings storage and acid mine drainage. Potential environmental impacts of these activities are managed through Protection of the Environment licencing by regulatory authorities.

Discrepancy between regulatory expectations of negligible impact and the practicalities of operating a large site can lead to conflict between mine operators and regulatory Authorities resulting in considerable financial and operational burdens placed on the Mine. Targeted scientific characterisation of perceived issues can resolve these differences and allow for practical and efficient resolution of contamination issues without operational disturbance to the mine.

METHODS

At a site in NSW, perceptions of groundwater contamination were triggered by PoEO monitoring conditions. As a result extensive additional drilling and monitoring was conducted to address perceived licensing issues without resolution of the effect on the environment at two operational areas.

We conducted a review of hydrogeological data and well construction, pumping tests, geochemical data analysis, critical review of previous reports and inspection of the site by senior experienced hydrogeologists. This allowed us to develop advanced hydrogeological conceptual models for the affected areas and thereby an improved understanding of the actual impact to groundwater. This allowed alleviation of the regulatory pressure which was being applied.

RESULTS AND DISCUSSION

Fractured rock groundwater environments are the target zone of many mining operations and often have complex hydrogeological behaviour, and natural background concentrations of target contaminants influenced by the inherent mineralised nature of the mine geology. This can lead to misperceptions about what constitutes contamination.

It is vital to differentiate between impact contained within the mining lease, and impact potentially affecting those outside the lease area, as well as confined aquifer response to changes in surface loading (aquifer compression). Accurate, robust, defensible and scientific analysis of these aspects of mine sites will aid in managing the nexus between active mine sites and contaminated land philosophy.

UTILIZATION OF BIOWASTES FOR MINE SPOILS REHABILITATION

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INTRODUCTION

Globally, around 0.4 x 10^6 km^2 area of land is estimated to be disturbed by mining activities, thereby contributing to severe environmental consequences including the generation of large amounts of mine spoils. The shortfall in topsoils, low level of organic matter and high heavy metal concentrations have been identified as the common problems in rehabilitation of mining spoils which can adversely impact the microbial activity and subsequent revegetation progression.

Biowastes, such as poultry and animal manure, biosolids, papermill sludges and municipal solid wastes (MSW) can be used to rehabilitate mine spoils. These biowastes provide a source of nutrients and also act as a conditioner to improve the fertility of spoils. Additionally, biowastes act as a sink for reducing the bioavailability of metal(loid)s in mine tailings through their effect on the adsorption, complexation, reduction and volatilization of metal(loid)s.

This paper provides (i) a general overview of the sources and global generation of biowastes, (ii) benefits of biowastes in terms of improving physical, chemical and biological properties of mine spoils, and (iii) current regulations of biowastes utilization. In addition, future research needs and strategies will be identified in terms of sustainable biowastes utilization in mine spoil rehabilitation.

METHODS

Currently available data were evaluated to assess the sources and quantities of biowastes generation in the global context. The potential carbon, nutrients and heavy metal contents of biowastes were calculated based on the recent published articles (Thangarajan et al., 2013). Existing regulations on biowastes management in the USA, Australia and Europe were considered in terms of understanding the adequacy for their usage in mine spoil rehabilitation.

RESULTS AND DISCUSSION

(a) Generation of biowastes and strength for spoils health

Large quantities of biowastes including poultry and animal manures, biosolids, papermill sludges and MSW are produced. For instance, the municipalities and water businesses generate MSW and biosolids as two major sources of organic wastes. It has been reported the global MSW production rate as at 1.3 billion tons in 1994 and it has risen by 31%, indicating a generation rate of 1.7 billion tons in 2008 (Foo and Hameed, 2009). This figure has been estimated to increase up to 2.2 billion tons with a rate of 1.42 kg/person/day in 2025 indicating their potential usage for mine spoil rehabilitation (Hoornweg and Bhada-Tata, 2012). The potential carbon and nitrogen from the Australian biosolids has been estimated as 163 and 12 tons for year 2013 indicating their potential nutritional values (Thangarajan et al., 2013).

(b) Retransformation of spoil architecture

It has been well understood and reported scenarios in application of biowastes on mine spoils rehabilitation since decades ago. The addition of biowastes to mine spoils restoring the ecosystem services under provisioning services (e.g., food and energy production);

regulating services (e.g., nutrients cycling and carbon sequestration); supporting services (e.g., water purification, pest and disease control); and cultural services (e.g., recreational experiences and scientific discovery) (Larney and Angers, 2012). Many field scale studies have demonstrated the directly and indirect benefits of biowastes for enhancing their receiving spoil environment. For instance, the intrinsic properties of biowastes indirectly reinforcing the chemical, physical and biological properties in receiving spoil soils has been reported in most instances (Allen et al., 2007).

(c) Regulations

A number of countries and organizations around the world have developed regulations for the application of biowastes in to agricultural lands and also for land rehabilitation. Most of these regulations have been focussed to avoid or minimize heavy metal contamination. Some of these regulations have been described the issues or guidelines related with pathogens and the emerging contaminants associated with biowastes such as sewage sludge. However, yet there has been no adequate comprehensive regulations on biowastes application and the effects of biowastes addition to the mine spoils rehabilitation.

(d) Implications; contaminants and their pollution

Recently, more concerns about soil and groundwater contamination have been reported in biowastes utilization for the remediation and revegetation of contaminated sites. For instance, mobilization of the leachable heavy metals (i.e., relatively poor retention of Ni by sewage sludge and leachable Pb complexes with water soluble organic matter by cattle manure) has been reported in some mine spoil rehabilitation cases (Andres and Francisco, 2008; Schwab et al., 2007). Greenhouse gases (i.e., CO_2, CH_4 and N_2O) emission through biowastes decomposition could be resulted as a major concern. However, proper management practices could be applied to avoid the demerits of biowastes utilization in mine spoil rehabilitation.

CONCLUSIONS

Biowastes improve mine spoil health by enhancing biological, chemical and physical properties of soils. However, contaminants and pathogens present in some particular biowastes such as biosolids could contribute to soil and groundwater contamination. Despite insufficient regulations on biowastes utilization in mine spoils rehabilitation, proper management practices of biowastes could be successfully applied to enhance the health of mine spoils. Future research on the potential of mine spoils as carbon storage sites though biowastes application is highlighted as an innovative frontier.

REFERENCES

Allen, H.L., Brown, S.L., Chaney, R., Daniels, W.L., Henry, C.L., Neuman, D.R., Rubin, E., Ryan, J.A., Toffey, W. (2007) The Use of Soil Amendments for Remediation, Revitalization, and Reuse, EPA Office of Superfund Remediation and Technology Innovation (OSRTI), US, EPA, Cincinnati, OH.

Andres, N.F. and Francisco, M.S. (2008) Effects of sewage sludge application on heavy metal leaching from mine tailings impoundments. *Bioresource Technol*. 99:7521-7530.

Foo, K.Y. and Hameed, B.H. (2009) An overview of landfill leachate treatment via activated carbon adsorption process. *J Hazard Mater*. 171:54-60.

Hoornweg, D., Bhada-Tata, P. (2012) What a Waste : A Global Review of Solid Waste Management, Washington, DC, USA.

Larney, F.J. and Angers, D.A. (2012) The role of organic amendments in soil reclamation: A review. *Can. J. Soil Sci*. 92:19-38.

Schwab, P., Zhu, D., Banks, M.K. (2007) Heavy metal leaching from mine tailings as affected by organic amendments. *Bioresource Technol*. 98:2935-2941.

Thangarajan, R., Bolan, N.S., Tian, G., Naidu, R., Kunhikrishnan, A. (2013) Role of organic amendment application on greenhouse gas emission from soil. *Sci Total Environ.* 465: 72-96.

REHABILITATION FUTURES FOR COALMINES IN THE HUNTER VALLEY

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INTRODUCTION

This paper reviews the evolution of issues pertinent to mine rehabilitation raised over the last five years at annual conferences on “Best Practice Ecological Rehabilitation of Mined Lands”, organised by the Tom Farrell Institute (TFI) and held in the Hunter Valley open-cut coal mining region. Attendance has been of the order of 200 delegates digesting some 15-18 presentations over the one day of the conference. Over the years this conference has become a venue for government, miners, environmental professionals, government representatives, scientists and community members to share recent research findings, policy updates and discuss best practice approaches to rehabilitation.

CHRONOLOGY

Coal mining in the Hunter Valley began in 1799 and indeed coal was the first commodity exported from the Sydney colony. Governor King famously wrote to Sir Joseph Banks in 1801: “*the first cargo of coals brought from the Coal River in a Government vessel I exchanged with the Master of the Cornwallis, who goes to Bengal…... Profit for our coals at two pounds five shillings per chaldron. I believe this is the first return ever made from New South Wales….. as such a produce ought not to be without some advantage to the Crown, I have regulated the export of that article”*

Most coal mining was underground and relatively unregulated in the early years. Indeed Newcastle now is a place where the high-rise builder must spend vast amounts of dollars to pour vast amounts of concrete into the disused shafts under the city to stabilise the foundations before the building can be built.

In NSW a Derelict Mines Program commenced in 1974 with the NSW Government allocating $125,000 to the rehabilitation of derelict mine sites where no individual or company can be held responsible for its management or rehabilitation. This has increased to over four million dollars for the 2014-15 financial year. Abandoned mines represent an ongoing problem for communities.

Open cut mining is now the preferred method of extraction with some 120+ million tonnes of coal being exported to an energy-hungry world through the port of Newcastle each year.

CURRENT ISSUES OF IMPORTANCE

Since 2011 at the annual “Best Practice Ecological Rehabilitation of Mined Lands” conference we have had many issues raised ranging from:

- The need to share the research and learnings required to determine ‘best practice’ rehabilitation and restoration of the mined land and stockpiled overburden. The importance of soil carbon and soil microbiota has become topical. Early-state ecosystems have been well documented but there have been few reports on ecosystem succession to achieve long term sustainability.
- The changes in planning approval requirements for restoration and community expectations of such endpoints. The social aspect of mine closure and rehabilitation is the hardest part of the process and also the most crucial.

- Legacy voids have become a very topical issue due to community realisation that across the Hunter Valley there may be as many as 30 voids occupying some 7000 to 10,000 hectares in decades to come.
  - Major concern relates to safety, stability and to water quality and the effects of the voids on ground water and associated rivers and streams.
  - Opportunities for future use are seen as an upside.

CONCLUSIONS

Uniformity of mining legislation across Australia would assist in bringing the best practices to mine planning, mining itself, mine rehabilitation and mine closure.

The economic case for future mines must include realistic mechanisms for financing the mine closure. Too many times the amounts factored into this equation have been inadequate to meet needs when the mine finally closes decades later, including taking into account the change in social license with time. It has been estimated that across Australia mining companies are potentially facing an unbudgeted rehabilitation liability of up to $17 billion dollars in achieving the mandated obligations for the closure of their mines.

Achieving successful closure, rehabilitation and reuse outcomes crucially rely on community engagement from the establishment of the mine through to closure. Such regional conferences as we hold in Singleton have perhaps their most significant function in bringing all players together in a networking environment.

REFERENCES

Governor King to Sir Joseph Banks (Banks Papers.), Historical Records of N.S.W., Vol.IV, pp.355, 359. by Bladen, F. M. C. Potter, Govt. Printer, 1892-1901, Sydney

RISK ASSESSMENT AND MANAGEMENT OF DERELICT MINES IN NSW

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INTRODUCTION

The NSW Government recognises that it requires a proactive approach to managing derelict mines in accordance with best practice industry standards. These standards are imposed to ensure human safety and that the integrity of the environment is maintained

Outstanding legacy issues surrounding over 550 derelict mines have the potential to cause immediate safety and environmental impacts as well as, that if not managed, potentially contributing to community misunderstanding of the sustainable life cycle of mining, and hence, be potentially damaging to the industry overall. As such, the Government understands that for current mining operations to attain a social licence and for the government to effectively regulate a sustainable mining industry, legacy issues must be adequately dealt with.

The Derelict Mines Program (DMP) with the Division of Resources and Energy (DRE) has recently finalised a risk assessment of all derelict mines across NSW. This risk assessment has then informed a works program that is being executed over the next several years.

The risk assessment developed and applied has placed the DRE in a position, where a prioritised work program, targeting safety and the environment simultaneously in the management of derelict mines will result in:

- the improved and successful management of derelict minerals sites throughout the state.
- establishing a team comprising of experts in land rehabilitation; ecology; contaminated site management; procurement, program and project management;
- establishing formalised systems and processes based upon international standards.

The NSW Derelict Mines Program (DMP)

Derelict mines are defined as mine sites that have historically not been satisfactorily rehabilitated, but no individual or organisation can be held responsible for their management. The potential risks posed by derelict mines to public safety and the environment. Essentially, derelict mines, are a legacy from historical operators before today's best practice regulation and mining practices incorporating environmental management and mine rehabilitation regulations were in place.

In the present, mine operators are subject to strict regulations so that all mines are rehabilitated, including security deposits mines lodge with the government to cover the costs of rehabilitation (if a company were not able to meet its obligations). Therefore, the cost of restoring the land is always borne by the mining company, not the NSW government and taxpayers. Current security held for mines in NSW exceeds $1.8 Billion.

To deal with historic mines sites, the NSW Department of Industry-Division of Resources & Energy (DRE) has developed and implemented a Derelict Mines Program (DMP). The program commenced in 1974 and now has an annual budget around of $3.5m for environmental rehabilitation and safety works. Projects are only considered for action by the DRE where no person or company with direct responsibility for the rehabilitation of the mine site can be located.

The selection of major projects for the DMP utilises a risk based approach to prioritising its operational program based on consideration of a variety of matters including:

- public safety risk presented by the derelict mine;
- environmental risk presented by the derelict mine;
- cost effectiveness of rehabilitation or remediation works.

However, a problem facing the DMP was the application of an up to date systematic evaluation of the status of derelict mines in NSW. Whilst the data mining of statutory reporting obligations of mines previous activities (data retained by DRE) is useful, the veracity of this data (reporting requirements at the time) limits this data set. This is a recognition that some mines that DRE is dealing with are over 100 years old.

DRE required an updated prioritisation of the potential actual impacts associated with Derelict Mines. For instance, there are several instances of derelict mines being unexpectedly encountered during land development. It was, therefore, paramount to have an update date and robust understanding of what derelict mines have the potential to significantly impact, and to what level, on public safety or the environment.

METHODS

Application of modern risk assessment methodology was utilised as the solution to the problem. The Risk Assessment-Prioritisation Project initiated by DRE was developed to understand the problem through compilation and updating of status (environmental and safety) within a database of all derelict mines in NSW. This dataset comprises of over 550 mines that have been determined to be derelict within NSW dating back to the 1800's.

The resulting safety and environmental risk assessments were designed to incorporate separate phases of review. This included an initial phase data analysis assessed in conjunction with a second phase site verification. This was based on information sources both historical as well as contemporary (which included data for a number of safety and environmental observations). The scope of the risk assessment and prioritisation project involved the following key phases:

- Detailed data reviews of all derelict mines in accordance with a set of safety and environmental criteria in order to high-grade a list of mines for site inspection
- Series of site inspections;
- Ranking of mines in order of risk against a set of risk criteria,

The risk assessment developed takes advantage of numerous data sets and interrogates them both independently and spatially to determine the relative risk rankings (safety and environmental) for remediation if required.

RESULTS AND DISCUSSION

DRE has successfully developed a methodology to rapidly assess a large number of derelict mines sites and to focus program resources. The assessment methodology developed in response to dated risk assessments (more than ten years old) ensures that projects are now prioritised in relation to the the highest risk sites across the state.

The methodology developed focussed on the approximately 550 sites in the construction of a derelict mines database. The methodology also utilised a data cleansing and ground truthing program for all higher risk sites. This process continually refines data held on sites and as more information becomes apparent, site risk profiles are updated.

The risk assessment methodology developed has been proven to be able to be deployed quickly as well as providing a quantitative, simple and systematic way in which all sites can be assessed and provides a relative prioritisation. The methodology and technology in the resulting new DMP database allows for flexibility in reporting and allows for reporting on individual risk themes. New sites are able to be rapidly ranked and pulled into the program. This is important when, for example, the newly identified sites are incorporated into the DMP.

CONCLUSIONS

DRE has successfully developed a quantitative assessment of the risks to public safety and to the environment on derelict mines within NSW. The assessment has provided a risk assessment score that has now been grouped into categories ranging from low to extreme risk to assist in management.

This has enabled a formalised and comprehensive compilation of data concerning the key potential safety and environmental hazards and the environmental sensitivity of the over 550 mines using both document and spatial databases as well as site visits and verification.

SCIENTIFIC ADVANCES AND INNOVATIVE APPLICATIONS IN ELECTROKINETIC REMEDIATION

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INTRODUCTION

The electrokinetic (EK) process has been considered as a viable and cost-effective technology for in situ remediation of subsurface contamination due to: (1) it works for geological matrices of low hydraulic conductivity such as clay and various sediments; (2) it works for inorganic contaminants, organic contaminants, and radionuclides; and (3) it is cost-effective (Acar and Alshawabkeh, 1993). More than 25 years ago the EK process had been demonstrated for remediation of soil and groundwater contamination in The Netherlands. In recent years significant technological advancements in application of EK remediation of various environmental matrices have been reported. This article aims to present a brief review of such advances from various perspectives.

LAB-SCALE STUDIES

Integration of the EK Process and Chemical Reduction Processes

To mimic the subsurface environment, a bench-scale horizontal column packed with nitrate-contaminated soil was treated by electrokinetic (EK) remediation coupled with the injection of nanosized Pd/Fe slurry (Yang et al., 2008). By injecting 0.05 wt% of the nanosized Pd/Fe slurry into the anode reservoir coupled with the application of an electric field resulted in over 99% of nitrate in the whole system was removed and degraded.

In a recent study (Gomes et al., 2015), a new experimental setup has been proposed using electrodialytic remediation and iron nanoparticles (nZVI) for remediation of soils contaminated with polychlorinated biphenyls (PCB). A historically contaminated soil with an initial PCB concentration of 258 mg/kg was treated during 5, 10, 20 and 45 d using different amounts of nZVI in both new setup (A) with conventional electrokinetics (setup B). PCB removal of 83% was obtained using setup A as compared with 58% by setup B. Setup A also showed additional advantages over setup B, such as a shorter treatment time, lower nZVI consumption, and about half of the voltage gradient requirement.

Integration of the EK Process and Advanced Oxidation Processes (AOPS)

The remediation performance of the injection of nano-Fe_3O_4 slurry coupled with the EK process for remediation of NO_3^- ($[NO_3^-]$ = 69.39–71.65 mg/kg) in a saturated sandy clay soil has been reported (Yang and Wu, 2011). The remediation results indicated that residual NO_3^-–N concentration of 1.35 mg/L in the anode reservoir was found to be lower than Taiwan EPA's Pollution Control Standards for Type I Groundwater Quality. In addition, a very low residual NO_3^- concentration in soil was detected. The relevant reaction behaviour obeyed the adsorptive reduction model proposed,

The effectiveness of nano-Fe_3O_4 activated persulfate oxidation coupled with the EK process for destruction of TCE in a spiked sandy clay soil has also been reported (Yang and Yeh, 2011). $Na_2S_2O_8$ was daily injected into the anode or cathode reservoir. The following findings were obtained: (1) Nano-Fe_3O_4 has been proven to be an effective activator for persulfate oxidation; (2) The cathode reservoir is the preferred location for injecting persulfate in this work. Under optimal conditions, the residual TCE concentrations in the soil specimen and electrode reservoirs all met the relevant control standards set by Taiwan EPA.

Further, nano-Fe_3O_4 activated persulfate oxidation coupled with the EK process for destruction of phthalates (PAEs) in river sediment has also been reported (Yang et al., 2015). Experimental results have demonstrated that under the selected operating conditions, 97.92% removal of di-n-butyl phthalate (DnBP) and 68.79% removal of di-(2-ethylhexyl) phthalate (DEHP) were obtained.

In a study ultrasonically enhanced electrokinetics (EK-US) tests were carried out to evaluate their performance on removal of the three persistent organic pollutants (POPs): hexachlorobenzene (HCB), phenanthrene (PHE) and fluoranthene (FLU) from kaolin (Pham et al., 2009). Among the three POPs, HCB was found to be the most difficult to treat.

PILOT-SCALE STUDIES

In a pilot-scale study conducted in South Korea (Jeon et al., 2015), the effectiveness of the solar-powered EK process for the remediation of As-contaminated soil collected from a former refinery plant was evaluated for its reduction in energy consumption over a test period of five weeks. Parallel tests were also conducted using a normal DC power supply system for comparison. Test results showed that the solar-powered system removed 27% of As and its counterpart removed 32% of As. However, the energy expenditure of the solar-based system was just 50% of its counterpart.

In a separate study by Hassan et al. (2015), solar cell panels were used as an alternative to generate the energy required for electrokinetic remediation of an artificially Cu-contaminated soil. The results showed that solar cell panels provided sufficient electric fields for electrokinetic remediation of soil contaminated with 355 mg of copper per kg of dry soil. A novel technique (Two Anode Technique or TAT) was proposed and investigated. The difference between this technique and the other innovative techniques is that this technique can reduce the operational involvement by personnel during electrokinetic remediation and thereby render the process more attractive and more economical. It was found that TAT was successful in removing about 75% of copper from soil, with the highest removal of 92% near the anode. Comparison of copper removal in the TAT tests and conventional anode-cathode (CAC) tests clearly illustrated that TAT was effective in combating the advancement of the base front and minimizing premature copper precipitation.

REFERENCES

Acar Y.B. and Alshawabkeh A.N. (1993) Principles of electrokinetic remediation. *Environ. Sci. Technol.* 27: 2638–2647.

Gomes H.I., Ottosen L. M., Ribeiro A. B., and Dias-Ferreira C. (2015) Treatment of a suspension of PCB contaminated soil using iron nanoparticles and electric current, *J. Environ. Manag*. 151: 550-555.

Hassan I., Mohamedelhassan E., and Yanful E.K. (2015) Solar powered electrokinetic remediation of Cu polluted soil using a novel anode configuration. *Electrochimica Acta* (Article in Press; http://dx.doi.org/10.1016/j.electacta.2015.02.216).

Jeon E.K., Ryu S.R., and Bake K. (2015) Application of solar-cells in the electrokinetic remediation of As-contaminated soil. *Electrochimica Acta* (Article in Press, http://dx.doi.org/doi:10.1016/j.electacta.2015.03.065).

Pham T.D., Shrestha R.A., Virkutyte J. and Sillanpaa M. (2009) Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin. *Electrochimica Acta.* 54: 1403–1407.

Yang G.C.C. and Yeh C.F. (2011) Enhanced nano-$Fe_3O_4/S_2O_8^{2-}$ oxidation of trichloroethylene in a clayey soil by electrokinetics. *Sep. Purif. Technol.* 79: 264–271.

Yang G.C.C. and Wu M.Y. (2011) Injection of nanoscale Fe_3O_4 slurry coupled with the electrokinetic process for remediation of NO_3^- in saturated soil: Remediation performance and reaction behavior. *Sep. Purif. Technol.* 79: 272–277.

Yang G.C.C., Hung C.H.; and Tu H.C. (2008) Electrokinetically enhanced removal and degradation of nitrate in the subsurface using nanosized Pd/Fe slurry. *J. Environ. Sci. Health A*. 43: 945–951.

Yang G.C.C., Chiu Y.H. and Wang C.L. (2015) Integration of electrokinetic process and nano-$Fe_3O_4/S_2O_8^{2-}$ oxidation process for remediation of phthalate esters in river sediment. *Electrochimica Acta* (Article in press; http://dx.doi.org/10.1016/j.electacta.2015.03.168).

AN EXAMINATION OF RECENT FIELD RESULTS FROM IMPLEMENTATION OF ELECTROKINETIC REMEDIATION APPROACHES IN LOW PERMEABILITY SOILS

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INTRODUCTION

The contamination of low permeability materials by chlorinated solvents and other recalcitrant compounds is a significant remediation challenge. The effective delivery of reagents using injection-based in situ remediation techniques can be limited by large differences in hydraulic properties, resulting in untreated compounds remaining in the low permeability material to act as a source to groundwater plumes. Electrokinetic-enhanced (EK-enhanced) delivery techniques, which rely on the electrical properties rather than the hydraulic properties of aquifer materials, have been demonstrated to improve delivery to low permeability materials. Rapid and uniform delivery of remediation agents such as oxidants and electron donors throughout low permeability materials in both homogeneous and heterogeneous environments using EK techniques has been previously demonstrated in both bench-scale and field-scale trials.

There are three different approaches to using EK enhanced delivery techniques currently applied in practice in the field. EK-Bio uses electromigration and electroosmosis to migrate lactate and microorganisms into contaminated regions. EK-TAP uses a combination of direct and alternating current to mobilize persulfate into treatment areas and then initiate the degradation reaction through resistance heating. EK-ZVI uses electrophoresis and the charged nature of nano-scale Zero Valent Iron (nZVI), to migrate this highly reactive particle into the target treatment area.

METHODS

A number of pilot studies are in operation in clayey-till source areas, where historical disposal practices have resulted in a significant presence of VOCs within the low permeability strata. Contaminants at the sites have entered the clay matrix through diffusion from numerous sand stringers, resulting in soil concentrations (within the very low permeability clay soil) greater than 1000 mg/kg in numerous locations. Results from a pilot test of EK-TAP and a full-scale implementation of EK-Bio at two sites in Denmark will be presented.

Danish clay tills are renowned for their ability to hold contaminants and the inherent difficulty in performing effective remediation of long-term contaminant sources locked within them. Two sites in Denmark are currently undergoing pilot or full-scale remediation using EK approaches. In both cases the contaminant consists of chlorinated ethenes, and has been shown to be resistant to more traditional remediation methods.

RESULTS AND DISCUSSION

The full-scale implementation of EK-Bio at the Denmark site is entering its third year of operation. Figure 1 presents the results of groundwater samples obtained from within the source zone from monitoring wells that intersect permeable sand stringers within the impermeable clay till. The results are presented in terms of degree of dechlorination (DOD) from the PCE parent (0% represents 100% PCE, 100% represents 100% ethene). Progress to less chlorinated daughter products of PCE is apparent with each cycle (application of electron donor) of EK.

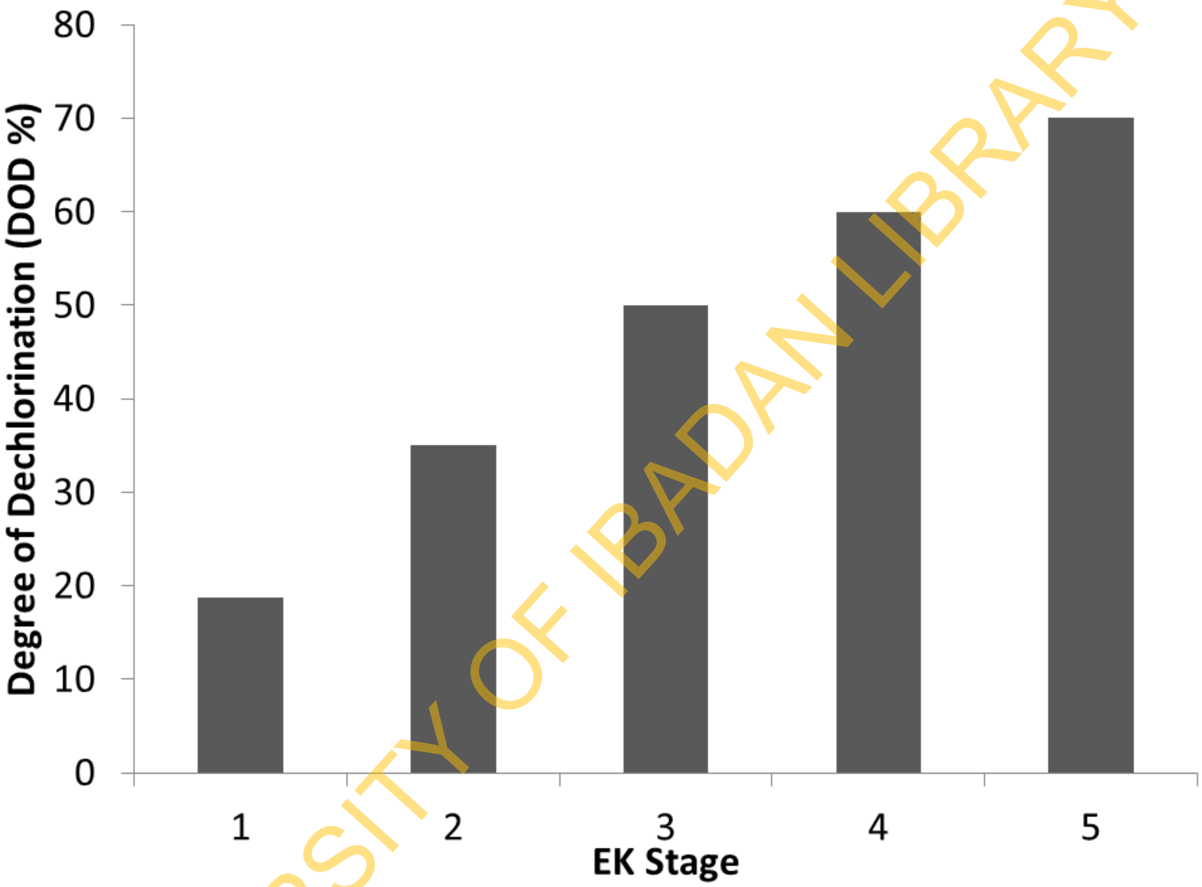

Fig. 1. Degree of Dechlorination of PCE parent in groundwater samples.

CONCLUSIONS

Intensive laboratory studies have demonstrated that EK-Bio and EK-TAP are promising approaches for remediation of low permeability or highly heterogeneous source zones. The world's first implementation of EK-Bio at full-scale has demonstrated that it is a highly efficient and cost-effective technique for remediation of low permeability soils acting as source zones to groundwater in more permeable regions. Several pilot-scale implementations of EK-TAP are currently underway, and represent the first time this technology has been demonstrated in the field. Although more challenging from an engineering standpoint, EK-TAP shows promise as an alternate EK-based approach for dealing with contaminants that are resistant to bioremediation approaches.

EVALUATION OF COMMERCIALLY AVAILABLE OXYGEN DISTRIBUTION TECHNOLOGIES

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INTRODUCTION

Naturally-occurring aerobic oxidation is limited by oxygen delivery rates in hydrocarbon-impacted zones. Enhanced aerobic bioremediation technologies focus on supplementing oxygen levels and can increase biodegradation rates by several orders of magnitude over non-stimulated rates. The balance between oxygen sources, oxygen uptake, and the degree to which oxygen is transported through the subsurface largely dictate the effectiveness of a bioremediation system.

This document reports the results of a side-by-side field evaluation of three commercially available oxygen distribution technologies: diffusion, ozone microbubble, and pulsed gas injection. Diffusion based oxygen distribution involves creating a high concentration of oxygen in an existing monitoring well, relying on the net movement of material across the concentration gradient to supplement areas of low oxygen content. Ozone microbubble systems employ micro-sized bubbles of air-encapsulated ozone, pulsed into the soil and groundwater at regular intervals to deliver oxygen/ ozone to the impacted area. Pulsed oxygen injection relies on regular discrete low-volume high-flow oxygen gas infusions into an impacted aquifer.

METHODS

Site

The evaluation utilized the National Environmental Technology Test Site program location at Naval Base Ventura County, Port Hueneme, California. This program provides well-characterized demonstration field locations for proof-of-principle, applied research, and comparative environmental technology demonstrations to facilitate transfer of innovative technologies to full-scale use. This test was performed in an area of the site with two distinct aquifers impacted with 0.5 to 1 mg/L methyl tertiary butyl ether.

Test Cell Arrangement

Three 20m by 20m test cells were created. Each test cell contained an injection location surrounded by at least 36 paired shallow (screened from 3 to 4mbgs) and deep (screened from 5 to 6mgbs) monitoring points corresponding to the shallower and deeper aquifer. Each technology was applied as per the manufacturer’s instructions.

Monitoring Protocol

Each well was sampled for oxygen concentrations monthly. Two baseline monitoring events took place prior to initiating the oxygen distribution technologies. After three months of operation, the technologies were stopped and oxygen levels were monitored for another three months to assess the stability and robustness of established zones of oxygenation. Technologies were then swapped to different test cells to verify results. Process control conditions were then varied to evaluate the operational envelope of each technology.

RESULTS AND DISCUSSION

Test cell groundwater oxygen concentrations were mapped for all monitoring events. Endpoints of 4, 8, and 16 mg-oxygen/L-groundwater were selected as the trigger concentrations for weak, medium, and strong aerobic signals.

Baseline Results

Initial oxygen concentrations from all three test cells were less than 2 mg-oxygen/L-groundwater for both baseline sampling events.

Diffusion-based Oxygen Distribution Results

Concentrations in the delivery well exceeded 40 mg-oxygen/L-groundwater during all three operational monitoring events. During the first and second operational monitoring events, no monitoring well groundwater concentration exceeded 4 mg-oxygen/L-groundwater. During the third monitoring event, a single well (0.5 m downgradient of the delivery well) in the shallow aquifer reported concentrations over 4 mg-oxygen/L-groundwater. No well in the deeper aquifer reported concentrations exceeding this trigger value.

Microbubble-based Oxygen Distribution Results

Concentrations in the delivery well were lower for this technology application, as the vendor-recommended approach was to run ambient air through a pressure swing adsorption unit to make ozone, effectively reducing the overall oxygen concentrations in the gas injected into the aquifer. The observed effective distribution was substantially larger than that for diffusion-based delivery methods, with a stable, robust plume of oxygen greater than 4 m diameter.

Pulsed Oxygen Distribution Results

The zone of effective oxygenation for this application was substantially greater than those observed for the other tested technologies, with a stable robust plume of oxygen exceeding 7 m diameter. Elevated groundwater oxygen concentrations were observed six weeks after cessation of injection. Figure 1 illustrates the effective oxygen distribution for the three technologies evaluated.

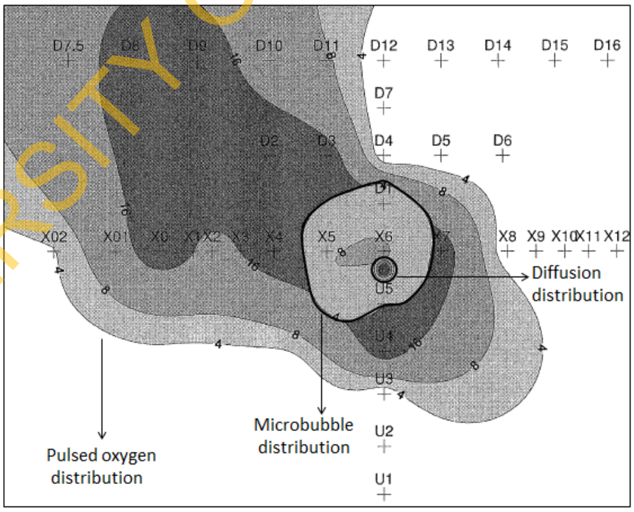

Fig. 1. Oxygen distribution results for three commercially available oxygen delivery technologies. All data are reported in mg-oxygen/L-groundwater.

CONCLUSIONS

These oxygen distribution technologies resulted in substantially different oxygenated zones. Oxygenated zones appear to be quite stable and do not appear to propagate in the downgradient direction in the manner advertised by many technology vendors. Oxygen die-away in well-established oxygenated zones appears to take several weeks, a circumstance with implications for aerobic remediation system operation and acceptable downtime.

PHYSICS BASED MANAGEMENT OPTIMIZATION (PBMO^{TM}) FOR WATER RESOURCE, ENVIRONMENTAL REMEDIATION AND DESIGN PROJECTS: THEORY AND APPLICATION

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INTRODUCTION

This paper discusses and demonstrates computational optimization technologies used for optimally managing environmental remediation project and programs by reducing remediation timeframes and costs. Those responsible for managing and implementing solutions for construction dewatering, dewatering for resource mining, sustainable public groundwater supply, and designing remedial design and operation projects are looking for tools that will help them find acceptable, efficient and effective solutions to complex and multi-faceted planning challenges at efficient cost points (Deschaine, 2014). At the project planning stage, optimal design develops the best technical approach and promotes better estimates of pricing and project scheduling, which translates into increased project execution success. Developing an optimal program and project design requires consideration of cost, benefit, technological readiness, project interaction and dependencies, programmatic and project level constraints on available funding, potential for increases and decreases for annual and total project and programmatic funding along with the uncertainty in both funding levels and the physical description of the subsurface environmental system. This paper demonstrates the technology and methods available that enable practitioners to simultaneously optimise a program while developing optimal investment strategies and operational solutions for individual projects with the transparency for stakeholders to review and accept them for use at both the planning and implementation stage.

METHODS

Deep understanding of optimization methods strength, applicability, and limitations, is important for developing successful implementations. Programmatic and project level implementation experience has shown that several predominant optimization methods exist that are routinely successful when deployed on projects. These methods are linear programming (LP), sequential linear approximation (SLA), and mixed integer non-linear programming (MINLP). These techniques are found applicable and efficient for a broad range of problems under consideration including single multi-objective optimization problems. Exhibition of case histories demonstrates value gained by using formal optimization was not obtainable by traditional subjective design methods.

Objective Function and Constraints

The fundamental requirement of single and multi-objective optimization is the development of a quantitative statement that describes the design objective to be minimized or maximized: an expression of system cost or performance as a function of the design elements as well as the constraints. (Deschaine, et. al, 2013).

Objective function: The objective function is a numerical formulation that includes one or more combination of fixed and variable costs that comprise of the construction, operation, maintenance, monitoring, and exit validation demonstration costs, the quantity to be optimized. The design can be predetermined, and the operations optimized, or the optimizer can optimize both the design and the operations simultaneously, including single and multiple management periods. The optimization method executes the model and uses the results to quantify the value of the objective function.

Constraints: The optimizer also determines whether the candidate design is feasible or not. Design feasibility consists of satisfying one or more constraint on the design or its performance (Deschaine, 2007). Constraint definition includes, but is not limited to:

(a) Design element activity such as the minimum or maximum abstraction rate of individual wells; their time of operation; aggregate pumping rate for one or more wells; maximum number of wells; balance between injection and abstraction rates)
(b) Design element location (location of abstraction wells and infiltration basins)
(c) Simulation results evaluate constraints at a location (point) or over a region (areal) regarding hydraulic head, hydraulic gradient, groundwater table drawdown, land surface subsidence, contaminant concentration; timeframe, GHG emissions, etc.)
(d) Derived simulation results (management, containment or capture of plume migration).
(e) Annual and total funding levels

Each candidate solution is fully evaluated. If all constraints are satisfied, the design is considered feasible, and the new cost is compared to the current "best" cost to see if the current design has improved the objective function value or not. Failure to satisfy one or more constraint yields an infeasible solution. Infeasible candidate designs provide valuable information to share with stakeholders that can pedagogically improve problem formulation.

RESULTS AND DISCUSSION

The PBMO method is demonstrated on a selected suite of industrial problems which includes the following project-level problem types the programmatic tool in demonstrated on a source selection funding example. In each case, the solution from the PBMO methodology exceeded the subjective engineering solution when available for comparison.

(a) Groundwater flow control for optimal construction dewatering
(b) Groundwater hydraulic plume containment using particle tracking
(c) Groundwater plume remediation of remedy-in-place (RIP)
(d) Groundwater plume remediation of RIP plus one new floating location abstraction well to minimize cost or maximize mass removal over a specified time frame
(e) Groundwater plume remediation of RIP plus two new floating location abstraction wells and three new infiltration basins to minimize cost over an unspecified time frame
(f) Programmatic source selection which formally and simultaneously includes subject matter expert individual and team opinions, limits on total funding, requirement to have a balanced program across technical investment areas, and stochastic optimisation to maximize portfolio value (benefit) whilst constraining downside thereby preventing escalating commitment to a failing course of action.

CONCLUSIONS

The PBMO methodology is tested and validated on a broad range of industrial projects. The methodology produces solutions that meet or exceed the best available solution either in use or proposed by a subject matter expert: $2.2M for a single project, and; $18M/yr for a program. Simultaneously combining programmatic and project level optimisation enables optimal design and implementation of environmental remediation response

REFERENCES

Deschaine, L. M. (2014). Decision support for complex planning challenges. Ph.D. Dissertation, *Chalmers University of Technology*, Göteborg, Sweden. 233p.

Deschaine, L. M., Lillys, T. P., & Pintér, J. D. (2013). Groundwater remediation design using physics-based flow, transport, and optimization technologies. *Environmental Systems Research*, 2(1), 1-21. http://www.environmentalsystemsresearch.com/content/pdf/2193-2697-2-6.pdf

Deschaine, L. M (2007) In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies, Chapter 9. *Interstate Technology and Regulatory Council*, 173p. www.itrcweb.org/Guidance/GetDocument?documentID=11

SOCIETAL PERCEPTIONS AND ACCEPTABILITY OF REMEDIATION TECHNOLOGIES

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INTRODUCTION

In recent decades the remediation of contaminated land and ground water has been marked by considerable technological innovation. Whilst the development and deployment of these technologies is driven in part by remediation experts, their deployment is also influenced by how they are perceived (e.g. risk or benefit) and accepted within broader societal contexts. This presentation will highlight some of the key findings from a CRC CARE research project examining the public's perceptions and acceptance of different remediation technologies. These research findings are drawn from a survey conducted with over 2000 residents who live in the vicinity of a range of contaminated sites in Australia, and involves discussion of the application of different technologies – physical, chemical, bio, and thermal - that could be used to remediate land and groundwater contamination at these sites. The findings are innovative in that they provide the first insights into various factors, including age, gender, levels of trust, through to location of technology application (e.g. in situ, ex situ) that determine residents' perceptions and acceptance of particular remediation technologies.

Whilst broader research has been carried out on societal acceptance and perceptions of technologies, few studies have focused specifically on remediation technologies, and very few have compared the public's responses to a broad cross-section of remediation technology types. The presentation concludes with a discussion of how these findings might be used to inform remediation policies and engagement strategies for contaminated land and groundwater.

METHODS

Findings within this presentation are based on a 20-minute survey (average time) used to collect data from members of the public living near or at 13 contaminated sites in New South Wales, South-Australia, Australian Capital Territory, Tasmania, Queensland and Victoria.

The survey was conducted using a computer-assisted telephone interviewing (CATI) software application, and used a random fixed-line telephone poll of 2009 adult residents living near or at the 13 Australian sites. Most respondents were asked about multiple remediation technologies, so there were 3966 responses in total to questions about remediation technology. Before the data was analyzed using regression, the data was subjected to pre-processing in which we examined the correlation matrix of responses, and made adjustments to eliminate highly correlated variables. Dependent variables for the regressions were technology acceptance and perceptions (e.g. misuse, risk), and independent variables ranged from socio-demographic characteristics through to trust and remediation technology types.

RESULTS, DISCUSSION AND CONCLUSIONS

The regression analysis revealed a range of significant relationships between the perceptions (e.g. concerns about misuse, risk) and level of acceptance of remediation technologies held by members of the public and a range of factors including their age, income, language, housing tenure type, the way in which they seek information, levels of trust, attachment to place, through to their predispositions. These significant findings support broader technology research which has already highlighted that the acceptance and perception of technologies is influenced by a number of factors including trust (Siegrist and

Cvetkovich 2000, Siegrist, Wiek et al. 2007), sense of place (Bickerstaff and Walker 2001), cultural and political dispositions (Kahan, Braman et al. 2009), socio-demographic variables, such as gender, age, income and education (Hoban 1998, Williams, Brown et al. 1999, Bodmer 2000, Siegrist 2000, Morton and Duck 2006, Ho, Scheufele et al. 2011), and housing tenure type (Wachinger, Renn et al. 2013). The presentation concludes with a discussion of the relevance of these findings to remediation principals (e.g. waste hierarchy), policies and engagement strategies.

REFERENCES

Bickerstaff, K. and G. Walker (2001). "Public understandings of air pollution: the 'localisation' of environmental risk." *Global Environmental Change* **11**(2): 133-145.

Bodmer, W. (2000). *The Public Understanding of Science*. London, Royal Society.

Ho, S. S., D. A. Scheufele and E. A. Corley (2011). "Value Predispositions, Mass Media, and Attitudes Toward Nanotechnology: The Interplay of Public and Experts." *Science Communication* **33**(2): 167-200.

Hoban, T. J. (1998). "Trends in consumer attitudes about agriucltural biotechnology." *AgBioForum* **1**(1): 3-7.

Kahan, D. M., D. Braman, P. Slovic, J. Gastil and G. Cohen (2009). Cultural cognition of the risks and benefits of nanotechnology, Nature Publishing Group. **4:** 87-90.

Morton, T. and J. M. Duck (2006). "Enlisting the Influence of Others: Alternative Strategies for Persuasive Media Campaigns." *Journal of Applied Social Psychology* **36**(2): 269-296.

Siegrist, M. (2000). "The influence of trust and perceptions of risks and benefits on the acceptance of gene technology." *Risk Analysis* **20**(2): 195-203.

Siegrist, M. and G. Cvetkovich (2000). "Perception of Hazards: The Role of Social Trust and Knowledge." *Risk Analysis* **20**(5): 713-720.

Siegrist, M., A. Wiek, A. Helland and H. Kastenholz (2007). Risks and nanotechnology: the public is more concerned than experts and industry, Nature Publishing Group. **2:** 67-67.

Wachinger, G., O. Renn, C. Begg and C. Kuhlicke (2013). "The Risk Perception Paradox—Implications for Governance and Communication of Natural Hazards." *Risk Analysis* **33**(6): 1049-1065.

Williams, B., S. Brown and M. Greenberg (1999). "Determinants of trust perception among residents suroudning the Savannah River Nuclear Weapons Site." *Environment and Behavior* **31**: 354-371.

REAL RISK VERSUS PERCEIVED RISK IN THE REMEDIATION INDUSTRY

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BACKGROUND

The remediation industry brings with it many unique hazards, including potential exposure to various hazardous substances. The perceived risk to health when working in this industry alongside contaminated material can vary from person to person. How does the real risk to occupational health differ from the perceived risk to health on contaminated sites? This paper provides strategies to educate key stakeholders to push the focus towards those tasks that result in a higher risk, rather than those in which a high risk is merely perceived.

METHODS

This paper will use case studies from two remediation sites, HMAS Platypus Remediation Project and the Former Macdonaldtown Gasworks Remediation Project, both previous gasworks sites in NSW. The paper will discuss the perceived risk alongside the real risk to health calculated on these projects and the strategies used to educate the workforce and key stakeholders on these risks.

It will discuss the process involved to determine the real risk to occupational health and the methods used to decipher appropriate controls. A review of example data and training will be presented to demonstrate the advantages to this overall approach.

RESULTS AND DISCUSSION

Qualitative Occupational Health and Hygiene Assessments (QOHA) were conducted for both projects which enabled high-level controls to be focused on areas where they were most needed. In addition to such controls, comprehensive training was rolled out to communicate and provide information on the contaminants of concern, their health effects and the controls in place to protect occupational health. The effectiveness of controls in place was determined through ongoing monitoring, which was communicated on a regular basis. Such a program enabled transparency for workers to understand their risk of exposure and to alleviate fears they may have experienced in relation to site works.

CONCLUSIONS

This paper reviews the real versus the perceived risk on contaminated sites and discusses options for educating workers and key stakeholders to ensure that control measures are focussed on where they are needed the most. Examples from two remediation sites in NSW are presented to demonstrate how this approach can be effective.

REFERENCES

AIOH 2006, *Simplified Occupational Hygiene Risk Management Strategies, A Guidebook for use in the Australian work environment on how to meet the Australian Safety and Compensation Council's requirement for employers to identify, assess and control risks arising from workplace exposures.*
Safe Work Australia 2011a, *Workplace Exposure Standards for Airborne Contaminants*
Safe Work Australia 2011b, *Code of Practice, Managing the Work Environment and Facilities*
Safe Work Australia 2012, *Guidance on the Interpretation of Workplace Exposure Standards for Airborne Contaminants*

ENHANCING RISK COMMUNICATION: IDENTIFYING INTEGRATION MECHANISMS BETWEEN EMPIRICAL SCIENCE, SOCIAL SCIENCE AND THE HUMANITIES

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INTRODUCTION

Risk communication is an essential aspect of life in the 'information age' and as a practice, takes many forms. This presentation draws upon some key literature in risk communication theory and describes research findings from an interdisciplinary literature review about communicating remediation risks and benefits to different groups of people.

THE RESEARCH PROJECT

The literature review is part of a doctoral research project about perceptions and attitudes to risks associated with the remediation of contaminated sites. The research explores the relationship between remediation experts and non experts. It aims to identify why misunderstanding may occur between them and find out how this situation may be improved.

RISK COMMUNICATION MODELS AND RESULTS OF AN INTERDISCIPLINARY LITERATURE REVIEW

For the remediation industry in Australia, risk communication often takes place during social engagement processes about technologies designed to destroy, minimise or control polluted soils and sediments, including those contaminated by Persistent Organics Pollutants (POPs). (UNEP, 2002). For this research project, risk communicators are experts in various fields associated with remediation. The people with whom they communicate are non-experts, and comprise members of the local community within which the remediation project has been, is being, or may be undertaken. A variety of factors influence how non experts perceive techno-scientific knowledge, including their level of trust in institutions and experts (Earle et al., 2007) and also their life experience (Washington et al., 2006).

Over the past forty years, a number of sentinel pollution events and industrial accidents greatly sharpened public interest in the health risks associated with exposure to hazardous chemicals.(Weir, 1986) (Van Den Bosch, 1978). A key driver of this changing social consciousness were the emerging impacts of POPs, including the insecticide DDT (Carson, 1963) and the industrial contaminant dioxin. The use of chemical defoliants during the Vietnam Way drew world attention to this highly hazardous substance (Evatt, 1985) as did the Seveso accident in 1976. (Warner M et al., 2011). The following decade saw further catastrophic accidents, including Bhopal as well as heightened visibility about the potential health impacts of exposure to pollution from contaminated sites in the US (US EPA, 2013) and the Union Carbide/Homebush Bay in Australia (Rubinstein and Wicklund, 1991).

Scientists commonly seek to address public concern about the risks posed by industrially-born phenomena, reasoning that more information is the antidote to the public's lack of trust in them. This approach is often called the deficit model of risk communication and has been found to have significant limitations. For example, research found that the provision of a lot of technical information could undermine trust in expert knowledge, rather then enhance it (Poortinga and Pidgeon, 2003). Hence, although the deficit model may have solid foundations in empirical science, is not considered adequate to explain risks associated with pollution destruction to non-experts.

A more nuanced approach is called 'the mental model' which was developed from psychology and focuses on values, experience, perception and the relationship between the cognitive and sensory functions of the human mind (Slovic et al., 2001). The other broad category is one that focuses on people-to-people relationships and emphasises inclusion, participation, dialogue and narrative (Susskind and Field, 1996). It is known as the dialogue model and, like the deficit model is widely practiced in Australia, in a variety of forms.

This presentation draws out some key aspects of these models as they apply to remediation and then provides some results from an inter-disciplinary literature review of writing from empirical science, social science and the Humanities. By taking this broad approach, the review identified a number of mechanisms that appear to be associated with improved risk communication. These have been called 'integration mechanisms' and include the use of imagery and narrative.

CONCLUSION

With media communications so strongly reliant on imagery and narrative, communication about remediation that ignores this reality may be at a disadvantage. This finding suggests that a research focus about the nature of the connections between separate disciplines may support improvements in risk communication about beneficial, but potentially hazardous, POPs destruction technologies.

This research is part of a doctoral study project supported by CRC CARE. The author thanks CRC CARE for the support provided to allow her to contribute to Clean Up 2015.

REFERENCES

BEDER, S. & SHORTLAND, M. 1992. Siting a hazardous waste facility: the tangled web of risk communication. *Public Understanding of Science,* 1**,** 139-160.

CARSON, R. 1963. *Silent spring,* Lond., H. Hamilton.

EARLE, T. C., SIEGRIST, M. & GUTSCHER, H. 2007. Trust, Risk Perception, and the TCC Model of Cooperation. . *In:* SIEGRIST, M., EARLE, T. C. & GUTSCHER, H. (eds.) *Trust in Cooperative Risk Management: Uncertainty and Scepticism in the Public Mind. .* London: Earthscan.

EVATT, P. 1985. Royal Commission on the use and effects of chemical agents on Australian personnel in Vietnam. Canberra AGPS.

POORTINGA, W. & PIDGEON, N. F. 2003. Exploring the Dimensionality of Trust in Risk Regulation. *Risk Analysis,* 23.

RUBINSTEIN, N. & WICKLUND, J. 1991. Dioxin Contamination of Sediment and Marine Fauna in Homebush Bay. Sydney: State Pollution Control Commission.

SLOVIC, P., FISCHHOFF, B. & LICHENSTEIN, S. 2001. Facts and Fears: Societal Perception of Risk. *Advances in Consumer Research*

SUSSKIND, L. & FIELD, P. 1996. *Dealing with an angry public: The mutual gains approach to resolving disputes* The Free Press.

UNEP 2002. Stockholm Convention on Persistent Organic Pollutants (POPs). Geneva: United Nations Environment Programme.

US EPA 2013. Superfund Remedy Report.

VAN DEN BOSCH, R. 1978. *The Pesticide Conspiracy*, The University of California Press.

WARNER M, MOCARELLI P & SAMUELS S, E. A. 2011. Dioxin exposure and cancer risk in the Seveso Women's Health Study. *Environ Health Perspect. ,* 119**,** 1700-1705.

WASHINGTON, S., ROZIER, P. & GOODALL, J. 2006. *Echoes from the Poisoned Well: Global memories of Environmental Injustice*.

WEIR, D. 1986. *The Bhopal Syndrome. Pesticide Manufacturing in the Third World,* Penang, IOCU.

ENVIRONMENTAL AND SOCIETAL MANAGEMENT OF CONTAMINATED LAND IN NIGERIA: THE NEED FOR POLICY AND GUIDANCE CHANGES

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INTRODUCTION

In recent years contaminated land management has become a major concern in Nigeria. While water and air pollution have received the most attention, the regulatory system for contaminated land remains largely undeveloped. As a result, there is an absence of: a clear and well-established policy framework; administrative structure and capacity; technical methods; and incentive structures. A reason for this is the lack of an effective environmental management framework. Without these instruments the ability of Nigerian courts to settle issues about environmental degradation is limited, and therefore, environmental issues are often settled elsewhere. In countries with robust environmental frameworks, e.g. the United Kingdom, contaminated land issues are dealt with using risk-based approaches. The need for risk-based oil spill management in Nigeria has been widely acknowledged (UNEP, 2011), however, to date only few regulatory instruments have been developed and promoted in Nigeria for contaminated land management in Nigeria. The current contaminated land regulation is poorly enforced and ineffective as the regulatory framework itself is fragmented and not well coordinated by governmental agencies.

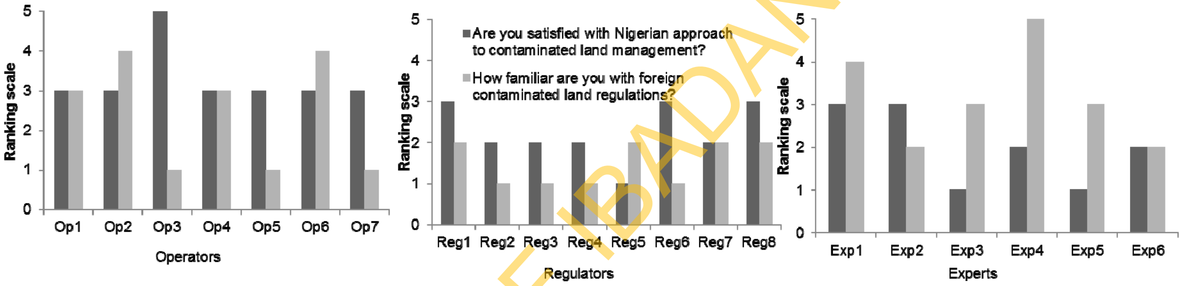
Here we provide a critical review of risk based contaminated land management practices in Europe and the USA. In addition, we compare the drivers for contaminated land regulation decisions across Nigeria, UK and USA. Finally, we present the results of our investigation into stakeholders' perceptions and satisfaction with the current contaminated land management regulation to understand the key aspects that need revision or inclusion.

METHODS

A critical scoping review of the legislative context of soil and water contamination across UK, USA and Nigeria was carried out to provide an overview of recent practice linked to the risk-based land management in the global context. The search covered conference and peer review journals, regulation, and reports. Overall 55 articles were reviewed. Further to this, a semi-structured interview (Yin, 2014) comprising 18 open and 5 closed ended questions was carried out to assess the stakeholders' acceptability and satisfaction with the current contaminated land management regime in Nigeria. A total of 21 interviews were conducted between July and December 2014. Respondents to the survey included experts in contaminated land remediation, regulators, operators, and local population. Each interview focused on three key aspects relating to: (1) factors that influence contaminated land management decisions in the region; (2) awareness and satisfaction with the current regulation; (3) knowledge of foreign contaminated land regimes. These questions were further explored using probing questions that were intended to achieve greater depth and clarity in the answers. A systematic and objective approach was used to describe, quantify and analyse written (transcribed) data as described by Krippendorff (2012) to identify the key concerns that individuals had on the three aspects mentioned above.

RESULTS AND DISCUSSION

Contaminated land legacies in the UK and the USA are due to many decades of industrial activity. The UK and USA contaminated land management regimes have evolved over three-decades of experience and are supported by evidence-based decisions. This is in contrast to Nigeria where the contaminated land legacy is more recent (from 1958 onwards), and thus, regulations are still developing. For example, the current management framework for contaminated land lacks statutory definition for contaminated land, options appraisal, structured risk assessments, and sustainable remediation. The UK and the USA have adopted liability regimes, standard land use, and technical strategies to identify and characterise contaminated land in terms of source-pathway-receptor (S-P-R) linkages. To understand how Nigeria can develop a better policy, we investigated respondents' satisfaction with the current regime in Nigeria and their knowledge of foreign contaminated land regimes that would benefit the regime in terms of policy transfer. Responses received indicate that: (i) drinking water quality, soil quality for farming, fishing and health and safety are the priority aspects that need to be addressed and included in contaminated land management decisions in Nigeria. There remains an urgent need for developing environmental and human health standards; (ii) the majority of respondents are unsatisfied with the current contaminated land management regime (Fig 1). This is likely due to the inability of the current policy framework and regulators to effectively prevent new contamination, as well as to clean-up existing problems. Overall, the operators are substantially satisfied with the current regime mainly due to poor enforcement by the regulators which seems to be beneficial to the operators; and (iii) the respondents have limited insight into the foreign contaminated land management regimes and this limits the their capacity to understand on how policy transfer can be adopted and transferred to Nigeria.



(1 = not all; 2 = a little; 3 = moderately; 4 = somewhat; 5 = considerably)

Fig 1. Stakeholders' satisfaction level of the current regime and knowledge of foreign regime

CONCLUSIONS

Contaminated land management in Nigeria needs to be revised. Currently, the governance structure for contaminated land management is complex and poorly coordinated. For contaminated land management to be successful in Nigeria, strong regulatory tools to enforce policies and provide a better working relationship between regulatory agencies need to be developed. Thus, a clearer regulatory policy supported by a holistic and coordinated governmental agency with the relevant technical expertise and resources is needed. Furthermore, a revised technical strategy to identify and characterise contaminated land in terms of S-P-R linkages, the establishment of a liability regime, and the development of risk criteria for land use are also required in Nigeria. These aspects of policy can be gleaned from the UK and the US experiences. Finally, evidence-based policy making that integrates environmental and social issues must be adopted. These processes are informed by science, expert knowledge, and public values.

REFERENCES

Krippendorff, K. (2012), *Content analysis: An introduction to its methodology,* Sage.
UNEP (2011), *Environmental Assessment of Ogoniland,* DEP/1337/GE, UNEP, Switzerland.
Yin, R. K. (2014), *Case study research: Design and methods,* Sage publications.

IS SEGREGATION OF BONDED ASBESTOS FROM SOIL CHEAPER THAN DIG AND DUMP REMEDIAL METHODS? –REMEDIATION OF ASBESTOS IMPACT IN UNCONTROLLED FILL IN URBAN NSW – A CASE STUDY

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INTRODUCTION

Asbestos containing materials (ACM) within soil are commonly found in urban environments throughout Australia. Historically a 'dig and dump' approach has been the primary remedial method with dealing with ACM impacted soils. A more quantitative risk based approach presented in the ASC NEPM (2013), allowed the adopting of a sorting and segregation strategy, rather than costly traditional 'dig and dump' remedial methodology.

The site comprised of 10 separate lots, and was formerly used for commercial purposes, mainly vehicle workshops and car sales yards. The former natural site topography was on sloping ground, so to provide a level site surface, fill had been bought to site at various stages over the past 80 years. In addition, there were several buildings containing ACM that were demolished in the 1970's to 1980's. The objective of the works was to remediate this 0.9ha urban site to a standard suitable for mixed commercial/residential land use, so that the site could be sold to a developer.

INVESTIGATION METHODOLOGY

Initial Assessment

Based on our knowledge of the 80 year developmental history of the site obtained from of a Phase 1 assessment, periods of fill activity were identified, allowing the site to be subdivided into zones of potentially different fill types. With reference to the ASC NEPM (2013) and WA DoH (2009) guidelines, the minimum number of sample locations required to characterise the entire site was in the order of 40. However, as we were focused on individual fill zones, additional test pits (77 test pits in total) were required to get a more accurate individual zone characterisation of ACM impacted fill and hence build a more robust conceptual site model.

Gravimetric sampling was used as recommended in the guidelines adopted. Several questions arose during gravimetric sampling, particularly to do with repeatability of results. Such as, was assuming a 15% asbestos content in fibro fragments always correct? Should a dry density of each sample be calculated? and how best to do so? What guidelines are to be compared against when loose fibres are detected? This presentation will look at how each of these aspects were addressed to ensure a consistent approach in the sample strategy, in order to provide as much comparability between results as this field test can provide.

Assessment Results

The results identified ACM distribution in fill that could be grouped into three broad categories:

a) Fill Type (a) - Pieces of bonded ACM (fibro and pipework) situated within a 0.2m vertical range in a buried topsoil layer. This zone was beneath former residential buildings (likely to have contained bonded ACM materials). The relatively orderly distribution of this ACM in this zone was associated with a one-off demolition event.

b) Fill Type (b) - Degraded fill soils with indiscriminate distribution of poor condition bonded ACM material (mainly fibro and vinyl tiles), friable asbestos (engine block gaskets), and asbestos Fines(bonded fragments <7mm) scattered throughout, some of which were found to be in poor condition. These were predominantly encountered in the vicinity of retaining walls across the site, and near a former fire damaged workshop.

c) Fill Type (c) - More recent (post 1970's) fill. In generally, bonded ACM pieces were less widely distributed, but where encountered, were in larger fragments (sometimes buried sheeting) that were in generally good condition.

REMEDIATION METHODOLOGY

Methods

To excavate and dispose of all the fill soils containing asbestos (estimated to be up to 7,000m^3) would be expensive. A decision was made to treat each of the different asbestos fill types differently, as follows:

a) Fill type (a) was raked using a tooth excavator bucket with two 90^o directional changes across grid sized areas (less than 10m x 10m). Pieces of bonded ACM (mainly fibro and pipework) were picked out by an asbestos removalist. Gravimetric soil validation sampling was carried out in each grid. If bonded ACM was still observed after validation sampling, either the racking and validation process was repeated, or a decision made to excavate and dispose the soil off-site.
b) Fill type (b) was excavated and disposed off-site. Due to the degraded quality of the ACM and presence of AF, these entire fill zones were removed en masse, rather than waste resources collecting validation samples in such poor quality fill were AF was bound to be detected in the sample.
c) Fill type (c) was coarse granular fill and was excavated under the full time supervision of a competent engineer and segregated into two stockpiles – one 'clean' and one 'contaminated', bucket by bucket. Fill pockets with large amounts of bonded ACM were placed into a 'contaminated' stockpile, and (on the basis of visual observations) remaining soils were placed in the 'clean' stockpile. Gravimetric soil validation sampling was undertaken as a final means of validating clean stockpiles.

Finally, the upper 0.1 to 0.3m of the ground surface was visually inspected for the presence of asbestos using racking with a toothed excavator bucket. This was undertaken twice - before and after a rain event- so as to ensure collection of as many remaining trivial ACM fragments as possible with a final surface clearance issued once no ACM was observed.

RESULTS AND CONCLUSIONS

Using the above methodology, the picking/segregation process allowed approximately 2000m^3 of fill soil to remain on-site and avoid offsite disposal, with potential savings of several hundred thousand dollars.

A key learning on sites which may have several distinct fill areas is to ensure that you have a robust conceptual site model, which may mean needing to consider the fill as separate zones prior to undertaking gravimetric sampling, and to also consider the fill source, reasons why a portion of the site may have been filled, and approximate age of the fill.

This lines of evidence approach also aids in developing a clear remedial strategy on how to target individual ACM impacted fill layers, and reduces the risk of under (or over) estimating asbestos impacted fill requiring off-site disposal at the remedial stage. This early upfront comprehensive characterisation will lead to overall cost savings rather than piecemeal 'on the run' assessments.

If a similar picking/segregation option is adopted, segregation is financially more economical as long as the rate of soil segregation meets a certain production rate, soil type is suitable (say soil volumes >25m^3 and a production rate of >25m3/day) which is highly achievable.

REFERENCES

National Environment Protection Council (NEPC) (2013). National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013, Schedule B1 – Guideline on Investigation Levels for Soil and Groundwater. National Environment Protection Council, Canberra.

Western Australian Department of Health (WA DoH) (2009). Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia. Western Australian Department of Health.

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THE THERMAL BEHAVIOUR OF RED MUD DURING HEAT TREATMENT AND UTILIZATION AS ADSORBENTS

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INTRODUCTION

Red mud as an industrial waste remains environmental concern due to its large volume generated and hazards impact to environment. Various utilization of red mud have been investigated, including producing building materials, development of adsorbents or catalysts, producing cement, utilized for rehabilitation or soil amendments and manufacturing functional polymers (Liu et al. 2011). Despite few field application being implemented, majority of the techniques are still struggling in laboratory for a cost-effective candidate. Similarly, most of the techniques would require certain level of pre-treatment or modification, such as neutralization, acid treatment and heat treatment. Heat treatment play an important role as for various utilization strategies. It's critical to understand the behaviour and transformation of metals in red mud during the treatment. Hence, in this study, the transformation of major elements in red mud, like Fe, Ti, Si, Al, during heat treatment with and without additives were investigated for future utilization of treated red mud as adsorbents. The information provided could be beneficial for developing its utilization strategies and minimizing waste materials.

METHODS

Red mud samples were collected from Rio Tinto Alcan Yarwun refinery, Australia (RRM). The sample were air dried and sieved to less than 2 mm prior to any treatment and analysis. The chemical and mineralogical composition of red mud are shown in Table 1. The RRM were heated at 200 - 600ºC for 2 h in nitrogen atmosphere (named as RMN200 – RMN600). Another part of red mud sample was mixed with sawdust (3:2 weight ratio) and 1:5 volume of MilliQ water, the mixture was incubated in end-over-end shaker for 24 days. The solid part (RMSDR) was obtained after centrifugation for calcination at 200 – 600ºC in same condition as RMN and the samples were named as RMSDN200 – RMSDN600 after calcination. The RRM, sawdust (SD) and RMSDR were analysed using TGA-IR system for investigating the thermal behaviour and transformation of minerals. The calcinated samples were analysed using XRD for their mineralogical composition together with RRM. Selected samples were analysed using SEM for morphological information and utilised for Cd and methylene blue removal in water.

Table 1. Chemical and mineralogical composition of samples

	Chemical composition (wt. %)				
Sample	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	Na_2O
RRM	34.48	22.53	13.88	6.84	9.41
RMSDN	32.19	20.59	13.15	6.38	7.48
	Semi quantification of minerals (%)				
RRM	Hematite(29), boehmite(12), anatase(5), calcite(7), sodalite(30), quartz (1), cancrinite (10), rutile (6)				
RMSDN600	Magnetite (40), sodalite (20), hematite (27), anatase (5), rutile (9), quartz (1)				

RESULTS AND DISCUSSION

Thermal behaviour

Several steps can be identified in weight loss from the differential thermal gravimetric (DTG) curves of RRM (Fig. 1(a)). In the pure red mud system, weight loss started with evaporation of physically absorbed water (2.92% from room temperature to 150ºC). The following weight loss peaks at 257°C and 338°C were attributed to loss of chemically absorbed water, mainly from the decomposition of structural water from boehmite and desilication products (sodalite, cancrinite, etc.) (Palmer and Frost 2009). Further weight loss occurred around 465-560°C peak at 520°C could be due to the further transformation of boehmite to transition alumina as the disappearance of boehmite peaks for RMN500 in XRD. The weight loss in the range 600–678°C peak at 653°C corresponding to the decomposition of carbonates (calcite) (Agatzini Leonardou et al., 2008). With presence of sawdust, the thermal stability of RMSDR is different from that of RRM (Fig.1 (b)). Significant amount of water evaporated in RMSDR which resulted in a weight loss around 50% below 100°C. The weight loss occurred at 317°C for both RMSDR and SD which was due to pyrolysis of sawdust components. This was confirmed by the generation of compounds containing $N(CH_3)_2$ (aliphatics), NOx (N_2O or NO), and CO_2 (IR spectra). Presence of C=O bond in aldehydes, ketones, carboxylic acids and esters were also identified from IR spectra (not shown). Further pyrolysis of sawdust occurred at around 365°C for SD which is absent for RMSDR and it may be due to the incubation during which compounds such as 2-pentanance, 4-hydroxy-4-methyl ($C_6H_{12}O_{12}$), Benzaldenhyde (C_7H_6O), and β-pimaric acid ($C_{20}H_{30}O_2$) were leached out by alkaline in red mud (analysed from liquid extraction). The third weight loss for RMSDR was found at 790°C, which account for 0.32% of the total weight. The last weight loss for both samples was found after 850°C, in which continuous generation of nitrogen oxides and carbon dioxide was shown by the IR spectra.

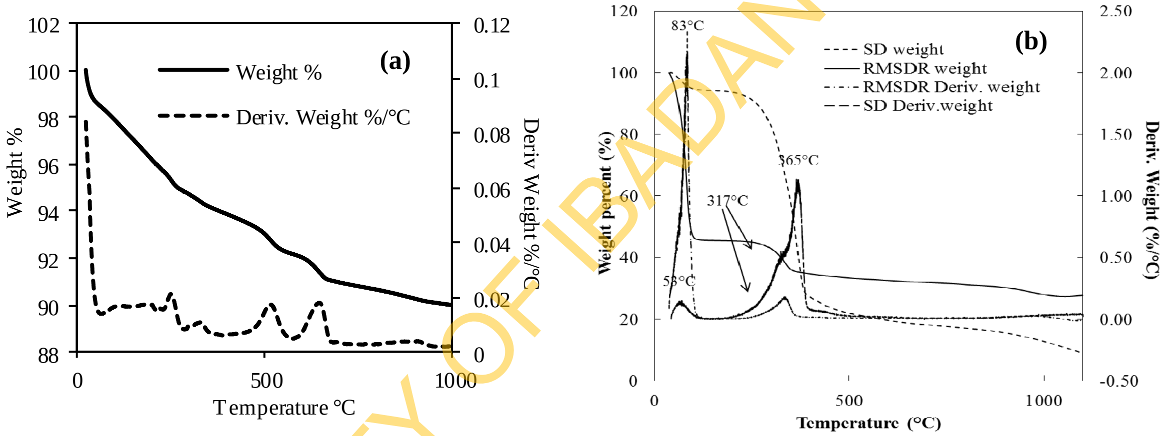

Fig. 1. TGA/DTG curve for (a) RRM and (b) SD and RMSDR

Mineralogical changes and utilisation

XRD analysis showed the decrease of beohmite peaks for RMN until totally disappear for RMN500. This confirmed the transformation of beohmite to some transition alumina which was difficult to confirm from XRD as in a complex sample. While for RMSDN samples, reaction occurred apart from the disappearance of beohmite peaks. Reduction of hematite by carbon materials occurred as decrease of XRD peaks for hematite and formation of magnetite peaks at 500°C.

The heat treated samples were used for simultaneously removal of Cd and methylene blue which showed 100% for both contaminants in a short period of time (24 h) for sample RMSDN while much lower efficiency by raw sample. This provided an option of utilization of waste red mud as adsorbents or soil amendments after heat treatment.

REFERENCES

Liu Y, Naidu R, Ming H. (2011) Red mud as an amendment for pollutants in solid and liquid phases. Geoderma 163:1-12.

Agatzini Leonardou, S., Oustadakis, P., Tsakiridis, P.E., Markopoulos C. (2008) Titanium leaching from red mud by diluted sulfuric acid at atmospheric pressure, Journal of Hazardous Materials, 157 579-586.

Palmer, S., Frost. R. (2009).Thermal decomposition of Bayer precipitates formed at varying temperatures, Journal of Thermal Analysis and Calorimetry.

CHEMICAL PROPERTIES OF SEAWATER NEUTRALIZED RED MUD IN RELATION TO REVEGETATION

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INTRODUCTION

Australia is the largest miner of bauxite and generates about 30% of the global alumina production. A major deposit currently being mined and refined is the Weipa deposit in northern Queensland. The Bayer process is used to extract alumina by dissolving bauxite in hot NaOH (Jones and Haynes, 2011). For every tonne of alumina extracted, 1-2 tonnes of alkaline, saline/sodic bauxite processing residues are produced. This residue is seawater-neutralized and then deposited in residue storage areas by semi-dry (30% solids) stacking between soil-based retaining walls. To date there are no reports on revegetation of seawater-neutralized mud residues. Residue sand (>150 µm), which is usually a minor portion of residue, is often separated from mud (<150 µm). Before revegetation the sand can be added to mud in the surface layer in order to improve aeration, drainage and root penetration (Courtney and Timpson, 2004).

The purpose of this study was to investigate the chemical properties of seawater neutralized residues and evaluate the effect of adding residue sand to mud on chemical properties of the substrate. The combinations used were: 100% mud, 75% mud/25% sand, 50% mud/50% sand, 25% mud/75% sand and 100% sand

METHODS

Bauxite residues were obtained from an alumina refinery, in northern Queensland, (derived from Weipa bauxites). The mud and sand were collected immediately following seawater neutralization and prior to their deposition in the residue disposal area. For each residue source, five treatments were prepared consisting 0:100, 25:75, 50:50, 75:25 or 100:0% v/v residue mud: residue sand. Samples (1kg dry weight) were thoroughly mixed, rewetted to 70% water holding capacity and incubated for four weeks. A subsample was air-dried for subsequent chemical analysis. Another subsample (200 cm^3) was transferred to polypropylene leaching tubes (12 cm long and 5 cm diameter). A plug of glass wool was placed at both the top and bottom of the incubation column to prevent loss of material by downward movement of fine particles during leaching. Samples were incubated for two weeks and then leached slowly (over a 24 hour period) with one pore volume of distilled water. Leachate was collected in polypropylene collecting containers and stored at 5 ºC until analysed. Following leaching, a tension of 17 kPa was applied to each column for 10 minutes to remove excess water. This process was repeated every 2 weeks for 7 leachings. At the completion of leaching, residue was removed from tubes and air-dried for subsequent chemical analysis.

Residues were subjected to a number of chemical analyses including mineralogical content by X-ray diffraction analysis, exchangeable bases by extraction with 1M ammonium acetate, cations in soil solution by saturation paste extraction, pH and EC by glass electrode.

RESULTS AND DISCUSSION

The main elements present in residues were Fe, Al and Si and the main crystalline minerals present were hematite, sodalite and goethite. The amorphous component made up 32 to 42% of the mineral content. Sodalite (also known as desilication product) is a sodium aluminium silicate mineral formed during the Bayer process which contributes to a slow release of Na^+ and OH^- ions from bauxite residues over time during storage (Barrow 1982).

This pool of residual alkalinity present in the residue in significant quantities means that although the residue was seawater neutralized to a pH of 9.3-9.4 compared to 11-13 for un-neutralized residues (Grafe et al., 2011) an increase in pH and exchangeable Na is likely to occur in the longer term, during storage. Due to seawater neutralization of the residues, they had a high EC and exchangeable Ca, Mg, K and Na content. Seawater neutralization causes the precipitation of soluble alkalinity as sparingly soluble Ca and Mg hydroxides and hydroxycarbonates (e.g. hydrotalcite) with a consequent decrease in pH (Hanahan et al., 2004). However, X-ray diffraction analysis did not detect crystalline compounds such as hydrotalcite suggesting they are present in non-crystalline form within the significant amorphous mineral content of residues. The EC values in saturation paste extracts prior to leaching were very high ranging from 28-34 dS m^{-1}. That is, an EC of > 2 dS m^{-1} is considered saline and values > 12 dS m^{-1} are generally considered too saline for most plants (Shaw, 1999). Such values underline the importance of allowing time for leaching of salts out of the profile prior to revegetation. The ESP after leaching ranged from 67-82% which suggests displacement and leaching of Na is also required.

Leaching caused a decrease in the EC of residues by at least one order of magnitude and ammonium acetate-extractable Na levels were reduced by more than half. The pH in leachates from residues increased progressively until they were about two units higher than initial values and the pH of residues also increased by about one unit. This was attributed to dissolution of solid phase alkalinity present in the residue. The increase in pH (of both the mud and of leachates) that occurred needs further investigation. In this regard, more emphasis needs to be directed towards characterizing the amorphous mineral component of residues particularly with respect to compounds that constitute residual alkalinity. Results suggest that prior to revegetation residues will need to be left to allow salts to leach out, after which gypsum will need to be added to displace exchangeable Na which can then be leached out.

REFERENCES

Barrow, N.J. (1982) Possibility of using caustic residue for improving the chemical and physical properties of sandy soils. *Aust. J. Agric. Res.* 33, 275-285.

Courtney, R.G.and Timpson, J.P. (2004) Nutrient status of vegetation grown in alkaline bauxite processing residue amended with gypsum and thermally dried sewage sludge – a two year study. *Plant Soil* 266, 187-194.

Grafe, M., Power, G. and Klauber, C., (2011) Bauxite residue issues: III. Alkalinity and associated chemistry. *Hydrometallurgy* 108, 60-79.

Hanahan, C., McConchie, D., Pohl, J., Creelman, R., Clark, M., Stocksiek, C., 2004. Chemistry of Seawater Neutralization of Bauxite Refinery Residues (red mud). *Environ. Eng. Sci.* 21, 125-138.

Jones, B.E.H. and R. J. Haynes, R.J. (2011) Bauxite processing residue: a critical review of its formation, properties, storage and revegetation. *Crit. Rev. Environ. Sci. Technol.* 41, 271-315.

Shaw, R.J., 1999. Soil salinity – electrical conductivity and chloride. In: Peverill, K.R., Sparrow, L.A., Reuter, L.A., (Eds.), *Soil Analysis: An Interpretation Manual.* CSIRO Publishing, Collingwood, Victoria, pp. 129-145.

REMEDIATION OF COMPLEX HAZARDOUS WASTES: HISTORICAL AND EMERGING CONTAMINANTS

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INTRODUCTION

Enviropacific are industry leaders in the treatment and management of complex hazardous wastes, allowing on-site reuse of treated material or disposal of treated wastes to landfill. This translates to significant cost savings for our clients. Hazardous waste is often complex, co-contaminated heterogeneous material. Managing these complex wastes requires a robust understanding of the contaminant chemistry and the treatment processes.

Enviropacific have successfully treated wastes containing a wide range of organic and inorganic complex contaminants, including both historical and emerging contaminants:

- Organic and organometallic contaminants: PFOS, PFOA and other perfluorinated compounds (PFCs), tributyl tin (TBT), gasworks and other industrial waste residuals (PAHs, TRH)
- Inorganic contaminants: cyanide, fluoride, hexavalent chromium, antimony, arsenic, cadmium, copper, lead, manganese, mercury, selenium, vanadium and zinc

METHODS

A key step to successful management of hazardous wastes is development of the treatment methodology by designing and conducting appropriate laboratory treatability trials. The laboratory tests allow development of the most suitable and cost-effective treatment methodology. Successful full-scale treatment of the waste material facilitates either application for specific immobilisation approval to the relevant state-based regulator, re-classification of the hazardous waste to meet reduced waste disposal criteria, or achieving on-site reuse criteria. For emerging contaminants such as PFOS and PFOA, development of screening assessment and trigger values for soil, surface and groundwater contaminated by PFOS and PFOA, and its remediation and treatment, is currently being undertaken by a National Policy and Technical Group.

RESULTS AND DISCUSSION

An overview of treatment methodologies developed by Enviropacific for a range of emerging and historical contaminants in various waste streams will be presented, together with an understanding of the treatment mechanisms involved. In particular, an overview of new treatment methodologies developed for soil and water impacted with PFCs will be presented.

Recent treatment trials conducted on impacted soils, sediments and water from two sites in Australia, have demonstrated highly effective chemical immobilisation of all 20 commonly observed PFC analytes, with >99% reductions of the major PFCs, and all minor PFCs reported as below laboratory detection limits.

The technology is based on chemical treatment and adsorption. The technology is straightforward, cost-effective and can be readily up-scaled to commercial application using mobile treatment equipment owned and/or designed by Enviropacific.

Table 1. PFC Soil Treatment Results

	PFOS*	PFOA*
Untreated (µg/L)	47.6	1.85
Treated (µg/L)	<0.02	<0.02
% reduction	>99	>99

*Toxicity Characteristic Leaching Procedure (TCLP)

Table 2. PFC Water Treatment Results

	PFOS*	PFOA*
Untreated (µg/L)	57.1	0.53
Treated (µg/L)	<0.02	<0.02
% reduction	>99	>96

Note: other PFCs in the suite of 20 commonly observed compounds were reduced to non-detect levels.

Full-scale Application

Water treatment

Enviropacific recently completed full-scale water treatment of PFCs at RAAF Williams Point Cook VIC, with over 16 million litres of water treated. The technology and equipment are well established, with the water treatment equipment designed to treat PFC contaminated water at rates of up to 10 L/s.

Soil treatment

The equipment used for the soil treatment process is a Hitachi Soil Recycler. The Soil Recycler is a track-mounted pug mill specifically engineered to provide high shear mixing for treatment of contaminated soils and sediments. The machine efficiently adds a variety of reagents with high accuracy to ensure adherence to specific immobilisation approvals and conformance. The throughput for the Soil Recycler ranges from 50 – 200 tonnes/hour, depending on soil type.

CONCLUSIONS

Contaminated soils, sediments, waters and industrial wastes are complex and often co-contaminated. They require a 'fit for purpose' solution to provide the most efficient and cost-effective treatment. Understanding the contaminant chemistry and treatment processes is key to their successful remediation.

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PROFILES AND REMOVAL EFFICIENCIES OF POLYCYCLIC AROMATIC HYDROCARBONS BY TWO SEWAGE TREATMENT WORKS IN HONG KONG

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INTRODUCTION

Sewage discharge could be one of the major sources of PAHs in water bodies. Stonecutters Island Sewage Treatment Work (SCISTW) and Shatin Sewage Treatment Work (STSTW) are two major sewage treatment works (STWs) in Hong Kong, adopting chemically enhanced primary treatment (CEPT) and biological treatment, respectively (DSD, 2009 a,b). The current study aimed at (1) determining the removal efficiencies of PAHs in the two major STWs (STSTW and SCISTW), (2) comparing the capabilities of the two STWs in removing PAHs, (3) characterizing the profile of each individual PAHs by evaluating their percentages in the total PAHs in the two STWs.

METHODS

Crude Sewage (CS), Primary Effluent (PE), Mixed liquor (ML), Dewatered Sludge (Cake), and Final Effluent (FE), were sampled in SCISTW and STSTW, respectively. The samples were collected once a week during the 5 weeks between November, 2011 and February, 2012. The well mixed liquid samples (CS, PE and FE) were separated into liquid portion (LP) and particulate matter (PM) by filtration (0.45 µm glass fiber filters). The freeze-dried filter papers, ML and Cake were then treated with accelerated solvent extraction (USEPA, 1996; Xia et al., 2011). Filtered liquid sample (1L) was extracted using solid phase extraction (SPE) method. Identification and Quantification of PAHs: Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene were conducted by a Gas Chromatography (GC). The analytical data for PAHs as reported for liquid samples and solid samples were re-evaluated based on flow analysis to deduce the (i) removal efficiency (RE) (total, sorption and biodegradation) and (ii) distribution profiles of PAHs during the sewage treatment process.

RESULTS AND DISCUSSION

The mean concentrations of total PAHs in raw sewage in STSTW and SCISTW were 300.96 ± 254.78 and 307.04 ± 217.43 ng/L, respectively, and Naphthalene (151.62 ± 31.86 and 149.81 ± 52.97 ng/L, respectively) contributed majority of the initial concentration of total PAHs. The concentrations of all individual PAHs decreased gradually along the treatment processes. It was found that STSTW was more capable in removing total PAHs (average TRE: 94.40 ± 4.12 %) than SCISTW (average TRE: 79.15 ± 7.48 %) ($p<0.05$) (Fig. 1). Nevertheless, no outstanding performance could be observed in the removal of some individual PAHs, including some probable human carcinogens (Group B2) (ATSDR, 1995), at STSTW (Fig. 1). At STSTW, secondary treatment performed better than the primary treatment, with regard to higher removal efficiencies in most of the individual and total PAHs. This could be mainly due to sorption of PAHs in particular matter but not biodegradation within the limited hydraulic retention time of sewage (about 10 h) in the bioreactor of STSTW (DSD, 2009b; Peng et al., 2009). This was further confirmed by the distribution coefficient (%) of individual and total PAHs in liquid (FE-T) and solid samples (Cake). A substantially greater portion of PAHs was detected in the solids than the liquid samples (Cake contained 92.5 and 74.7% of total PAHs in SCISTW and STSTW respectively, whereas FE-T contained 7.53 and 25.3% of total PAHs in STSTW and SCISTW, respectively). In the profiles of PAHs along the sewage treatment process from crude sewage to final effluent, a stepwise increase of low molecular weight (LMW) PAHs (Naphthalene – Anthracene) in percentages was noted at both STWs. This was probably attributed to the relatively lower log K_{ow} values of LMW PAHs and the sorptive characteristic of the more hydrophobic HMW PAHs (Wang et al., 2013).

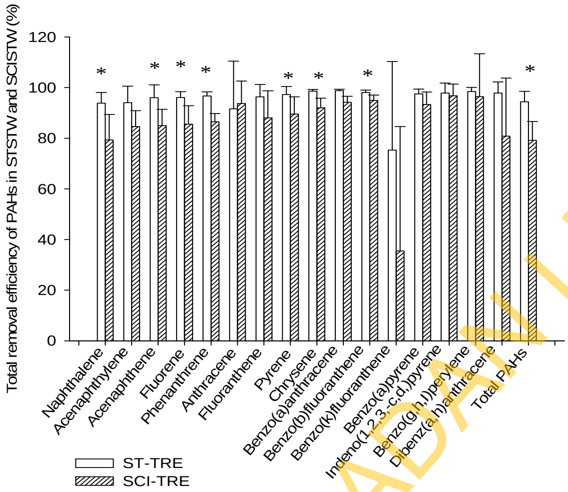

Fig. 1. The total removal efficiency (TRE) of individual and total PAHs at STSTW and SCISTW. Bars with asterisk (*) show significant difference between the total removal efficiencies of PAHs at STSTW and SCISTW according to T-test ($p<0.05$).

CONCLUSIONS

Despite the impressive capability of STSTW and SCISTW in removal of PAHs, there was still a considerable amount of total PAHs (1.85 and 39.3 kg/yr, respectively for the two STWs) being discharged into Hong Kong water regions, which would be an environmental concern. There is a need for improving the sewage treatment facilities in removing these contaminants and controlling the emission of PAHs to the local environment.

REFERENCES

ATSDR (Agency for Toxic Substances and Disease Registry). (1995). Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). U.S. DHHS, Atlanta.

DSD (Drainage Services Department). (2009a). Stonecutters Island Sewage Treatment Works.

DSD (Drainage Services Department). (2009b). Shatin Sewage Treatment Works.

Peng, X.Z., Tang, C.M., Yu, Y.Y., Tan, J.H., Huang, Q.X., Wu, J.P., Chen, S.J., Mai, B.X. (2009). Concentrations, transport, fate, and releases of polybrominated diphenyl ethers in sewage treatment plants in the Pearl River Delta, South China. Environ. Int. 35: 303–309.

US EPA (United States Environmental Protection Agency). (1996). Method 3540C: Soxhlet Extraction. US Environmental Protection Agency, Washington, DC.

Xia, C., Lam, J.C.W., Wu, X., Sun, L., Xie, Z., Lam, P.K.S. (2011). Levels and distribution of polybrominated diphenyl ethers (PBDEs) in marine fishes from Chinese coastal waters. Chemosphere 82: 18-24.

Wang, X.W., Xi, B.D., Huo, S.L., Sun, W.J., Pan, H.W., Zhang, J.T., Ren, Y.Q., Liu, H.L. (2013). Characterization, treatment and releases of PBDEs and PAHs in a typical municipal sewage treatment plant situated beside an urban river, East China. J. Environ. Sci. 25: 1281-1290.

ASSESSING CLEAN AND GREEN ENERGY FROM ORGANIC WASTE IN AUSTRALIA

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INTRODUCTION

A large volume (14 million tonne) of organic waste is generated in Australia. Currently most of such waste ends up into landfill generating greenhouse gas emissions, unless the biogas is trapped. Biomethane potential of different organic waste differs depending on the volatile solids and biodegradability. Though literature is available for biomethane potential from specific organic waste, it is always recommended to test the biomethane potential for the actual waste generated.

CRC CARE has commissioned an Automated Methane Potential Testing System –II (AMPTS-II) to assess the biomethane potential for different organic waste. This testing provides an idea about the embedded green energy in the organic waste streams. The data generated from such testing will provide an idea about overall energy generation and how effectively it can be utilised for the end user.

This paper describes energy potential from different organic waste streams carried in Australia which has been carried out on AMPTS-II system.

METHODS

Automated Methane Potential Testing System (AMPTS-II) supplied by Bioprocess Control Sweden was used for testing different organic wastes. The protocol provided in the operation manual is supplied by Bioprocess Control. The systems comprises of 14 individual bio-digeseter equipped with a motor and agitator. Temperature was maintained at 37°C during the testing period while the data generated from testing was downloaded once the biomethane production reached a steady state.

Assessed organic waste

The samples tested on AMPTS-II include livestock manure (piggery, cattle), mushroom waste and purpose grown biomass. The details of testing have been provided in Table 1.

Table 1 Testing details

Organic Waste	VS %	Temp, °C	S:I ratio
Piggery	1.99	37	1:2
Cattle	6.44	37	1:2
Mushroom	19.29	37	1:2

VS-Volatile solids , Temp.-Temperature, S:I substrate to Inoculum

For mushroom a combined waste of fresh compost, ageing compost and mushroom stalks was added with a proportion of 60:30:10 respectively, while the piggery and cattle manure was used as such.

RESULTS AND DISCUSSION

The data regarding accumulated volume (NmL) and flow rate of the biomethane (NmL/day) is recorded continuously in the flow cell unit. The biomethane volume generated from individual reactor is monitored and stored in the system's in-built software.

The volatile solid content of pig manure, cattle manure and mushroom waste represents 70%, 89% and 59% respectively. While previous samples analysed for livestock manure matches this data, the total solid concentrations vary depending on water usage.

The accumulated biomethane for pig manure, cattle manure and mushroom waste was found to be 2575 Nml, 1765 Nml and 1624 Nml respectively. With this biomethane accumulation, the BMP for pig manure, cattle manure and mushroom waste was found to be 443, 137 and 43 L CH4/gVS. This data is matching with the published reports for piggery (Asam *et al.*, 2011), cattle manure (Noorollahi *et al.*, 2015) and mushroom waste (Bisaria *et al.*, 1990).

During the anaerobic digestion process in the bio-digesters, a digestate is produced which has a nutritive value in terms of N, P, K and micronutrients. The digestate generated from these organic wastes had different nutrient levels.

CONCLUSIONS

Different organic waste tested showed that there is considerable embedded energy into such waste that can be harnessed further for direct combustion, electricity generation or vehicular fuel. Simultaneously the digestate generated from the process can be utilised as a source of organic fertiliser with an inherent N,P,K in the waste.

With number of livestock animals in Australia considerable energy as well as fertiliser can be generated that will not only save the fossil fuel but also reduce the greenhouse gas emissions.

REFERENCES

Asam Z.Z., Pulsen TG, Nizami AS, Rafique R, Kiely G, Murphy JD (2011) How to improve biomethane production per unit feestock in biogas plant Appl Energy 88(6): 2013-2018

Younes Noorollahi, Mehdi Kheirrouz, Hadi Farabi Asl, Hossein Yousefi, Ahmad Hajinezhad.(2015) Biogas production potential from livestock manure in Iran; Renewable Energy Reviews 50: 748-754

Ragini Bisaria, Padma Vasudevan, and V. S. Bisaria (1990) Utilization of spent agro-residues from mushroom cultivation for biogas productionAppl Microbiol Biotechnol 33:607-609

ASSESSMENT OF NITROGEN LOSSES THROUGH NITROUS OXIDE (N_2O) FROM A WASTEWATER IRRIGATED SOIL

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INTRODUCTION

Effluents from agricultural industry such as abattoir and dairy wastewater are significant contributors towards nitrous oxide (N_2O) emissions (Kampschreur et al., 2007). The land disposal of waste and wastewater is a major source of N_2O emission. This is due to the presence of high concentration of nitrogen (N) and carbon in the waste. For example, abattoir wastewater contains 217 to 250 mg/ L of N concentration and chemical oxygen demand (COD), 1057 mg/ L (Cassidy and Belia., 2005). Since N_2O is a greenhouse gas with high global warming potential, its emission from wastewater irrigation is likely to impact global climate change. Therefore, it is important to examine the effects of abattoir wastewater irrigation on soil for N_2O emission potential.

METHODS

The equivalent of 3 kg of abattoir wastewater irrigated soil was sieved and taken in a 4 L plastic container. Abattoir wastewater was used for irrigating the plants at the rates of 50 and 100 % field capacity (FC). Four crop species including alfalfa (*Medicago sativa*), mustard (*Sinapis alba*), maize (*Zea mays)* and sunflower (*Helianthus annuus*) were used with no crop serving as a control. The entire experiment was carried out with three replications.

Nitrous oxide emission was monitored using a close chamber technique. The chamber was placed inside the plastic container and N_2O emission was measured for seven days after the planting. A syringe and pre-evacuated vial were used for collecting the gas samples; a fresh and clean syringe was used each time to avoid cross contamination. The collected gas samples were injected to gas chromatography device immediately after each sampling to analyse the concentration of N_2O from different treatments.

RESULTS AND DISCUSSION

The overall N_2O emission was compared for all the crops under two different abattoir wastewater treatment rates (50 and 100% FC). Under 100% FC (wastewater irrigation), among the four species grown in the abattoir wastewater irrigated soil, *Medicago sativa* (16mg pot^{-1}day^{-1}), *Sinapis alba* (15mg pot^{-1}day^{-1}), *Zea mays* (15mg pot^{-1}day^{-1}) and *Helianthus annuus* (15mg pot^{-1}day^{-1}) showed higher N_2O emission compared to the 50% treatments - *Medicago sativa* (11mg pot^{-1}day^{-1}), *Sinapis alba* (10mg pot^{-1}day^{-1}), *Zea mays* (11mg pot^{-1}day^{-1}) and *Helianthus annuus* (11mg pot^{-1}day^{-1}). Similarly, pots with plants have shown 35 % less emission than the pots without plants. The N_2O emission of soil without plants at 100 % FC (19mg pot^{-1}day^{-1}) was higher than the 50 % FC (16mg pot^{-1}day^{-1}) (Figure 1). Similar trends of N_2O emission flux were observed between the irrigation period (4 weeks period) for 50 % FC and 100 % FC. Under the 100 % FC loading rate treatments, with the highest N_2O emission was in the following order week1 > week4 > week3 > week2. On the other hand, Under the 50 % FC loading rate treatments, the highest N_2O emission was recorded in the first few weeks and in the following order week1 >week2>week3 week>4 (Table 1).

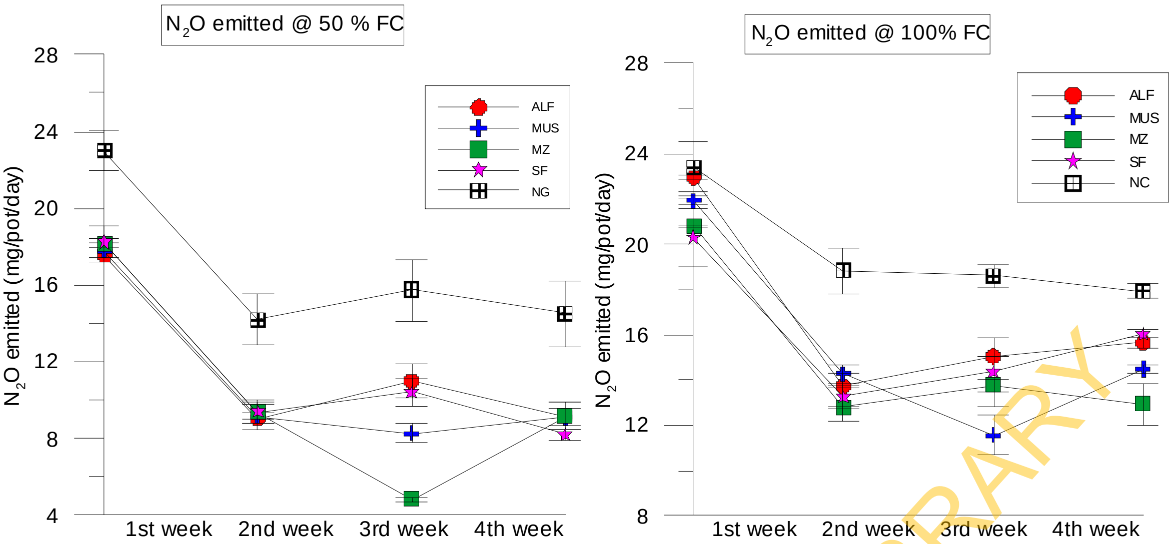

Figure 1. Nitrous oxide emission from soil irrigated with abattoir wastewater with 50 and 100% FC (moisture gradients) – measured at four week after planting. ALF: Alfalfa; MU: Mustard; MZ: Maize; SF: Sunflower; NC: No crop

Table 1. Effects of abattoir wastewater irrigation on N_2O emission (mean ± s.d. n=30); comparison of overall effects of two types of moisture gradient with four weeks of sampling (2 sample t –test).

N_2O emitted	50 % FC	100 % FC	Sig.diff.
Week 1	19±3.1	21.9±3	n.s
Week 2	10.2±2.8	14.6±4.9	$p<0.05$
Week 3	10.1±4.6	14.7±4.7	n.s
Week 4	10±4.9	15.4±2.4	$p<0.001$
Overall	49.3±12.5	66.5±9.3	$p<0.001$

n.s not significant

CONCLUSIONS

The main conclusions that can be drawn from this study in relation to plant induced denitrification are; N_2O emission rate increased with increasing soil moisture content; N_2O emission rate increased with increasing N input through wastewater irrigation; N_2O emission rate decreased with the presence of plants which can be attributed to plant uptake.

REFERENCES

Kampschreur et al., (2007) "Unraveling the source of nitric oxide emission during nitrification." Proceedings of the Water Environment Federation 2007.2 (2007): 843-860.

Cassidy and Belia, (2005) "Nitrogen and phosphorus removal from an abattoir wastewater in a SBR with aerobic granular sludge." Water research 39.19: 4817-4823.

USE OF FOOD WASTES TO REPLACE PART OF FISH MEAL IN FISH FEED PELLET FOR LOWING LEVELS OF MERCURY, DDTs AND PAHs IN CULTURED FRESHWATER FISH

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INTRODUCTION

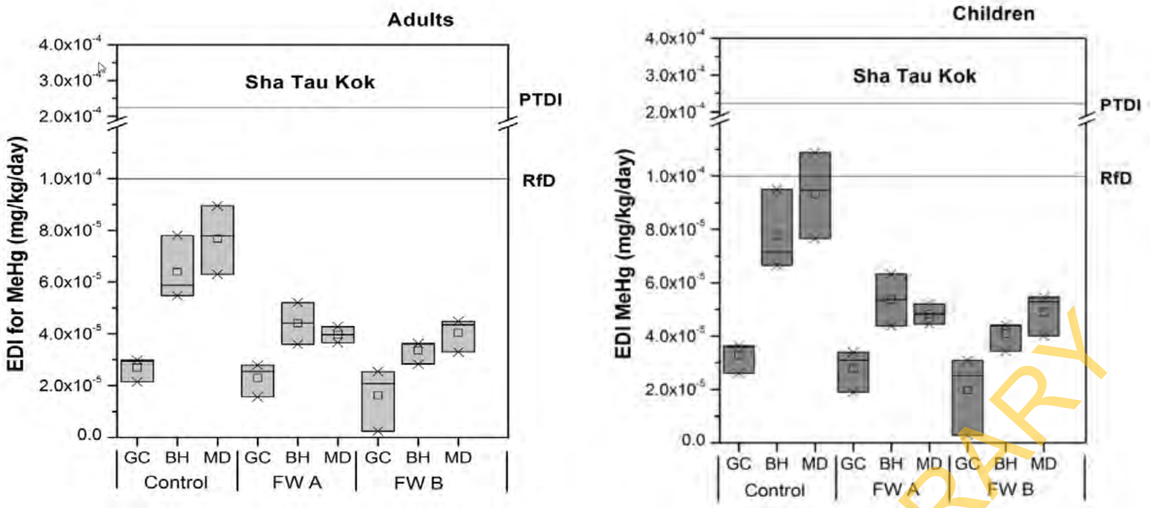
Fish meal derived from trash fish is the major source of protein for fish growth, but it is also the source of contaminants in commercial fish feeds. The major objective of this study was to investigate the feasibility of using food wastes to replace part of fish meal in fish feeds for lowering levels of contaminants in cultured fish, based on a field trial.

METHODS

After feeding 3 different fish species in the field for one year, with food waste pellets (FW A and FW B, with cereal and meat as the major ingredients, respectively) and a commercial feed (control), total and bioaccessible concentrations of methyl-mercury (MeHg), DDTs, polycyclic aromatic hydrocarbons (PAHs) in bighead carp (BH) (*Hypophthalmichthys nobilis*), grass carp (GC) (*Ctenopharyngodon idellus*) and mud carp (MD) (*Cirrhina molitorella*) were analysed (using gas chromatography-cold vapor atomic fluorescence spectrometer (GC-CVAFS) for MeHg, and Hewlett-Packard (HP) 6890 N gas chromatograph (GC) coupled with a HP-5973 mass selective detector (MSD) for DDT and PAHs). Human health risk assessments were conducted, based on body weight (BD) of 60 kg for an adult and 21.8 kg for a child to suit the local situation (Lee et al., 1994; Wang et al., 2005), and daily consumption rate of fish in Hong Kong of 93 and 50 (g/day) for adults and children, respectively (Leung et al., 2000).

RESULTS AND DISCUSSION

Based on the oral reference dose of 1.00E-04 (mg/kg/day) for total MeHg (US EPA, 2014), there were potential non-cancer risks for adults and children, via consumption of BH (83% and 100%, respectively) and MD (66.7% and 100%, respectively), fed with the commercial diet, but not the food waste based diet (FW A) and there was a potential non-cancer risk exerted on children via consumption of BH (33.3%), fed with FW B. However, there were no potential health risks obtained for total DDTs and PAHs contained in fish fed by all diets. The bioaccessible concentrations of MeHg, DDTs and PAHs were also determined using an *in-vitro* digestion model. For the bioaccessible MeHg, a potential non-cancer risk via consumption of MD (33.3%) fed with the commercial diet was observed for children (Fig. 1) No potential health risks were observed for bioaccessible DDTs and PAHs in fish exerted on human health. The results also indicated there were significantly lower health risks based on the levels of MeHg and DDTs in MD fed by FW A and FW B, compared with the control ($p<0.05$). Even though PAHs concentrations in MD fed by FW A and FW B were generally higher than those fed by the commercial feed ($p>0.05$), the PAHs levels in fish were considered to be safe for human consumption.



Note: RfD= reference dose (1.00E-04 mg/kg/day) (US EPA, 2014); PTDI= provisional tolerable daily intake (2.29E-04 mg/kg/day) (JECFA, 2003). Each box represents the interquartile range (25th and 75th centile) of EDI of each fish. MD = mud carp; BC = bighead carp; GC = grass carp; Control = commercial pellets; FW A = food waste A; FW B = food waste B.

Fig. 1. Estimated daily intakes (EDI) of bioaccessible MeHg through consumption of freshwater fish by adults and children in Hong Kong.

CONCLUSIONS

There seems to be a great potential of using food waste-based pellets to replace commercial feeds for growing safe and quality freshwater fish based on the lower levels of MeHg and DDTs in fish fed by food waste-based pellets, compared with commercial feeds.

REFERENCES

JECFA (The Joint FAO/WHO Expert Committee on Food Additives). (2003). Summary and conclusions of the sixty-first meeting of the Joint FAU/WHO Expert Committee on Food Additives, 16-18. Joint FAO/WHO Expert Committee on Food Additives. World Health Organization, Geneva.

Lee, M.M., Wu-Williams, A., Whittemore. A.S., Zheng, S., Gallagher, R., Zhou, L., Wang, X., Chen, K., Ling, C., Jiao, D., Jung, D., Paffenbarger, R.S. (1994). Comparison of dietary habits, physical activity and body size among Chinese in North America and China. *Int. J. Epiddemiol.* 23: 984-990.

Leung, S.S.F., Chan, S.M., Lui, S., Lee, W.T.K., Davies, D.P. (2000). Growth and nutrition of Hong Kong children aged 0–7 years. *J. Paediatr. Child Health.* 36: 56-65.

Wang, X.L., Sato, T., Xing, B.S., Tao, S. (2005) Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *Sci. Total Environ.* 350: 28-37.

US EPA. (2014). Integrated Risk Information System (IRIS), Methylmercury (MeHg) (CASRN 22967-92-6). Wachington, DC: Enrionmental Protection Agency.

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NUTRIENT MANAGEMENT IN ABATTOIR WASTEWATER IRRIGATED SOIL — BIOMASS AND ENERGY PRODUCTION

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INTRODUCTION

In most developed countries including Australia, meat consumption is high resulting in the increase in number of abattoirs over the last few decades. Large quantity (150 to 225 GL/annum) of water is used for meat processing in abattoirs and almost the same volume is discharged containing high contents nutrients (N and P) and organic loads, which has the potential to cause eutrophication in water bodies (Phillips, 2002). Land application of the abattoir wastewater (AWW) is the most common low-cost method. While discharge to waterways cost more than $1.55/kL, discharge to land costs about $0.6/kL (Matheyarasu et al., 2013). Therefore, this paper discusses the potential use of plants to trap nutrients from AWW irrigated soil and utilise it towards biomass and energy generation.

AIMS OF THE PROJECT

While there are chemical- and bio-reactors which could clean up AWW, the costs involved in these processes are enormous (Obaja et al., 2005; Patil et al., 2010). Hence, this project aims to take up excess nutrients using plants, with the following specific objectives:

- To characterise the soil samples from wastewater discharged soil. The properties of soil provided the extent of contamination thereby helped in strategizing the entire research.
- To identify suitable high-biomass producing plants, which could uptake maximum N and P. The plants were grown in greenhouse and substantiated using field trials.
- To determine the energy value of biomass from field experiment and utilise them for electricity generation. Energy value of biomass was measured using CRC CARE's AMPTS anaerobic digestor and methane was analysed post digestion.
- To detail the cost of the remediation and to seek potential partners to extend the technique to large scale remediation of other sites beyond Australia (especially China).

In the plant growth experiments (greenhouse and field trials), plants such as giant reed, napier grass, alfala , maize, sunflower and selected native grass species were used. The removal of P from abattoir wastewater irrigated soil was demonstrated using flyash (FA) and redmud (RM) amendments; N removal using denitrification experiments.

RESEARCH FINDINGS

The samples collected from AWW irrigated site were analyzed for selected chemical parameters and the results are presented in Table 1. With the wastewater sample showing high C, N and P, the nutrients showed up higher in the AWW irrigated soil compared to control soil, thereby serving as a nutrient source for plant growth. Selected plant species were grown in greenhouse to estimate biomass production and also to determine N and P transformation in soil in the presence of plants. The overall biomass improved with increase in wastewater addition (Figure 1) and the results were confirmed with field trials.

Transformation of P in AWW irrigated soil (21 days incubation with FA, RM and control) was studied in the presence and absence of plants. The porewater P increased as the plant growth progressed (Figure 2a) and there was a negative correlation between porewater pH and P (Figure 2b). The plant grown soil, in the presence of amendments, showed high oxalic acid activity resulting in increased Olsen P values (Table 2) and higher biomass production.

Table 1 Chemical properties of wastewater and soil samples

Properties	Wastewater	Control soil	Irrigated soil
pH	7.59±0.11	8.51±0.12	6.63±0.08
EC µS/cm	2686±15.50	1709±12.38	5036±21.07
Total C	223.17±1.76[a]	14525±67.28[b]	15523±73.56[b]
Total N	418.9±3.42[a]	647±6.21[b]	1400±20.83[b]
Total P	212.1±1.98[a]	107±0.97[b]	281±4.89[b]
Olsen P	-	8.63±0.22[b]	62.16±0.54[b]
Soil type	-	Calcarosol	Calcarosol
Texture	-	Loam	Loam

[a] expressed as mg/L; [b] expressed as mg/kg

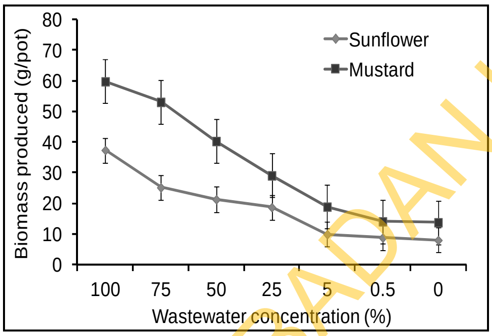
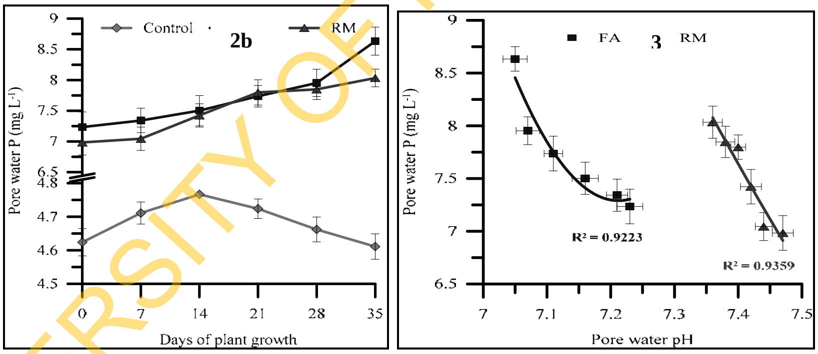


Figure 1 Biomass production



a b

Figure 2 Relationship between porewater P and (a) plant growth, (b) porewater pH

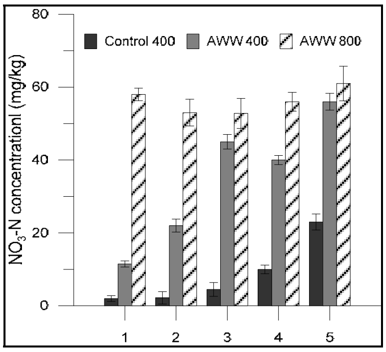


Figure 3 NO_3-N concentration in soil; 1-Sunflower, 2-Alfala, 3-Maize, 4-Napier grass, 5-Giant reed

Biomass of giant reed and sugarbeet produced from field trials were anaerobically digested and methane (CH_4) was analyzed. Results showed that sugarbeet root (Figure 4) produced maximum CH_4 compared to other feedstocks, indicating its potential energy value.

Table 2 NO_3-N concentration in soil

Samples	Initial OA (mmol kg^{-1} soil)	Soil incubation			Plant experiment		
		Final OA (mmol kg^{-1} soil)	% increase	Olsen P (mg kg^{-1})	Final OA (mmol kg^{-1} soil)	% increase	Olsen P (mg kg^{-1})
Control	0.0121	0.0169	28.40	92.38	0.1031	88.26	102.17
FA	0.0143	0.0179	20.11	135.63	0.2942	95.13	153.61
RM	0.0132	0.0178	25.84	124.32	0.2863	95.38	137.47

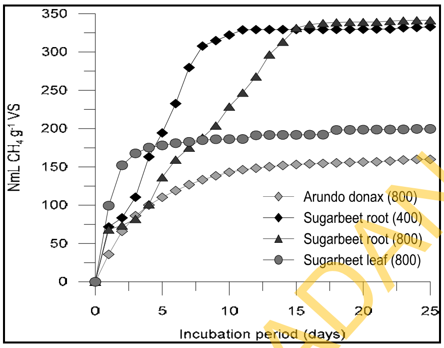


Figure 4 Methane production

CONCLUSIONS

Utilising land trapped nutrient resources without losing them to environment is challenging. By selecting suitable plant species to grow over the wastewater contaminated land, contaminants (N and P) can be effectively managed. Plants not only act as remediators, but also provide biomass that can be used for energy generation as evident from CH_4 produced.

REFERENCES

Obaja, D., Macé, S. and Mata-Alvarez, J. (2005) Biological nutrient removal by a sequencing batch reactor (SBR) using an internal organic carbon source in digested piggery wastewater. Biores. Technol. 96(1): 7-14.

Patil, S.S., Kumar, M.S. and Ball, A.S. (2010) Microbial community dynamics in anaerobic bioreactors and algal tanks treating wastewater. Appl. Microbiol. Biotechnol. 87: 353-363.

Matheyarasu, R., Seshadri, B., Bolan, N.S. and Naidu, R. (2012). Nutrient management in effluents derived from agricultural industries: an Australian perspective. WIT Transactions on Ecology and The Environment, 168, pp 213-223 (Eds. Bjornlund, H., Brebbia, C.A. and Wheeler, S.).

ALGAL BIOMASS AFTER BIOREMEDIATION — AN ECONOMICAL SOURCE FOR BIOSYNTHESIS OF IRON NANOPARTICLES

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INTRODUCTION

In recent years, synthesis of nanoparticles using biological sources including microalgae gaining importance as it overcomes the drawbacks of instability, high cost, use of toxic chemicals and generation of hazardous by-products. Though these nanoparticles are highly reactive, economically viable and environmentally safe, cultivation of microalgae involves the use of chemical fertilizers as nutrient source, high cost, supplementary energy and additional fresh water. Hence, in this study, an attempt was made to use brewery waste water (BWW) as a nutrient source for algae production. By this technology, biomass production along with remediation of waste water can be achieved (Rawat et al., 2011). To demonstrate this, we cultivated microalgae, *Chlorella* sp. using BWW and produced the iron nanoparticles using the algal biomass produced.

METHODS

Biomass production using brewery waste water (BWW)

Pure culture of *Chlorella* sp. MM3 was inoculated in characterized and processed BWW and incubated at 24^{O}C in an orbital shaker for 10 days. Aliquots were taken periodically and analyzed for algal growth by estimating optical density at 664nm (Farooq et. al., 2013).

Iron nanoparticle synthesis (FeNPs)

FeNPs were synthesized using algal biomass by treating with iron chloride and characterized using scanning electron microscope (SEM) for size and shape and energy dispersive x-ray spectroscopy (EDAX) for elemental composition (Subramaniyam et. al., 2015).

RESULTS AND DISCUSSION

The growth of MM3 grown in BWW medium were estimated in terms of optical density and represented as growth curve in fig 1. The lag phase and exponential phase during first four days clearly indicate the growth of MM3 in BWW medium and it attains a stationary phase after 4 days. Simultaneously, the nutrient content of BWW was found to be decreasing (Data not shown). This concludes that algae had natural adaptation of using nutrients from BWW to grow which is concurrent with results (Farooq et. al., 2013).

The 4 days old biomass were collected and washed with deionized water and incubated with iron chloride for nanoparticle synthesis. The SEM image confirmed the presence of spherical shaped iron nanoparticles of size 5-15 nm. The EDAX spectra confirmed the presence of iron along with carbon and oxygen which caps the nanoparticles. This is concurrent with iron nanoparticles produced using microalgae *Chlorococcum* sp. MM11 grown in BBM medium (Subramaniyam et.al., 2015).

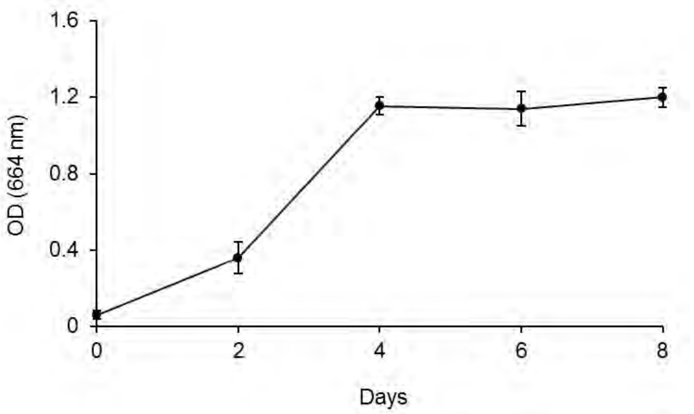

Figure1: Growth curve of Chlorella sp. MM7

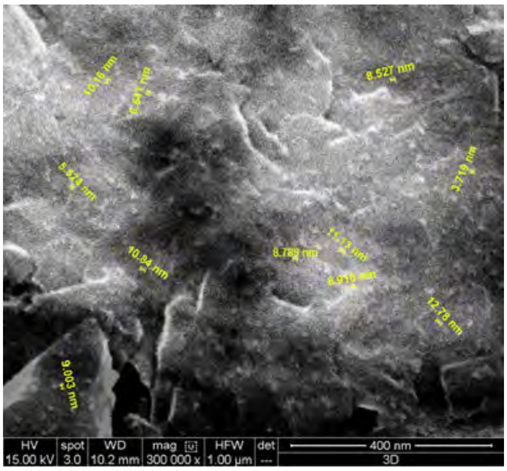

Fig 2: SEM image of FeNPs

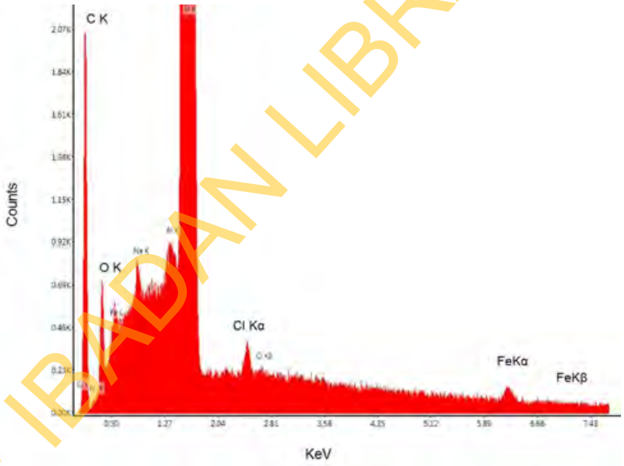

Fig 3: EDAX spectra of FeNPs

CONCLUSION

This study concludes that bioremediation along with biomass production will be a promising technology for the synthesis of iron nanoparticles economically.

ACKNOWLEDGEMENT

The authors acknowledge Australian Government and CRC-CARE for providing Scholarship, University of South Australia for research facilities and Coopers for providing BWW sample.

REFERENCES

Farooq, W., Lee, Y., Ryu, B., Kim, B., Kim, H., Choi, Y., Yang, J. (2013) Two-stage cultivation of two Chlorella sp. strains by simultaneous treatment of brewery wastewater and maximizing lipid productivity. *Bioresource Technology.* 132: 230–238.

Rawat, I., Kumar, R.R., Mutanda, T., Bux, F. (2011) Dual role of microalgae: phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. *Renew. Energy,* 88: 3411–3424.

Subramaniyam, V., Subashchandrabose, S.R., Thavamani, P., Megharaj, M., Chen, Z., Naidu, R. (2015). *Chlorococcum* sp. MM11—a novel phyco-nanofactory for the synthesis of iron nanoparticles. *Journal of Applied Phycology*, 1-9.

SITE CONTAMINATION PRACTITIONERS AUSTRALIA CERTIFICATION SCHEME: THE FIRST 10 MONTHS

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INTRODUCTION

Ten months have passed since the launch of Site Contamination Practitioners Australia (SCP Australia), and the certification scheme it manages. SCP Australia is the direct result of calls from the contaminated site sector for a benchmarked accreditation process across Australia to improve the quality of work being delivered by practitioners. The scheme has been made possible through the financial and operational contributions made by CRC CARE. The aim of certification is to augment and support the accredited auditor scheme operating in various Australia states and to encourage continuing professional development in the area of contaminated site assessment and management.

The launch of the scheme in late November 2014 was the culmination of two years consultation led by CRC CARE with industry, regulators and consultants on why certification is needed, and the types of competencies contaminated land practitioners should demonstrate to achieve certification. A great deal of consultation was invested in developing the scheme blue print, and the challenge of implementation has provided the opportunity to refine and calibrate both understandings and expectations of certification in the contaminated site sector.

DISCUSSION

Since November SCP Australia has established itself, conducted a full assessment round and has been engaged in promoting certification amongst practitioners and promoting the brand amongst stakeholders and end users. This poster will review feedback from the accredited environmental auditors who acted as assessors for the first round, who implemented the SCP Australia defined standard for practitioner certification. The poster will include exerts from the Chief Assessor's report, as well as an overview of applications received for certification.

This poster will present the six key competencies at the heart of the scheme developed through the consultation process. These are the consolidated product of repeated consultations with industry, consultants, and regulators on what stakeholders believe are the key competencies required of practitioners at a certified level. Feedback from end users and their expectations of the scheme will also be related. The scheme is designed to be a practitioner's scheme and not just for consultants, with best practice the benchmark in delivering outcomes for end users.

This poster is a consolidated reflection of SCP Australia to date, the vision for the scheme, the challenges and lessons learned as SCP Australia continues into its first year of operation.

SOIL SCIENCE AUSTRALIA'S CONTAMINATED SITE ASSESSMENT AND MANAGEMENT CERTIFICATION FOR SOIL SCIENTISTS

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INTRODUCTION

Contaminated land assessment and remediation is a complex multi-disciplinary area, which draws on experts in a range of fields (e.g. hydrogeology, risk assessment, community consultation) including, on the vast majority of sites, soil science. It is internationally recognised that soil science is a highly specialised field. An individual providing advice in any field of soil science must be suitably qualified i.e. a Certified Professional Soil Scientist.

Soil Science Australia (SSA) provides accreditation for suitably qualified members as Certified Professional Soil Scientists (CPSS). Accreditation as a CPSS requires applicants to satisfy the Standards for Professionals in Soil Science, comply with SSA's Code of Ethics and Rules of Conduct, and demonstrate on-going professional development. The CPSS scheme defines the educational qualifications and professional competences required of a professional soil scientist.

The CPSS Accreditation Board have developed Specialised Competencies (comprising "Core Knowledge" and "Practice") within CPSS which have been driven by regulatory requirements for competent assessment of soils for various industries – one of these is Contaminated Site Assessment and Management (CSAM). All of the Specialised Competencies are only available to CPSS members, who adhere to the rigorous professional standards maintained by the CPSS Board and who attain a minimum of 50 hours per year of continuing professional development.

Soil Science Australia acknowledges other schemes are available for general contaminated land professionals and a unified scheme is unlikely. CPSS is differentiated from these other general schemes by being a specialised certification, which has been developed and maintained by SSA, the peak body for soil scientists.

This paper will examine the key regulations and guidance of the different State settings and will expand to examine international practices on accreditation of soil scientists, particularly in applied and multi-disciplinary fields such as contaminated land. A critique will be provided in relation to the certification schemes available both in Australia and internationally which accredit individuals to provide advice on soil science.

This paper is particularly relevant to those setting standards who are currently debating the future of the contaminated land industry; to practitioners who work across State boundaries; and also site owners considering using the skills of a soil scientist.

CONTAMINATED GROUNDWATER MONITORING NETWORK DESIGN DEDICATED TO REDUCE UNCERTAINTY

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INTRODUCTION

In contaminated groundwater systems, the characteristics of contamination sources are identified using contamination concentration measurements collected in the field, using an arbitrary or predesigned monitoring network (Amirabdollahian & Datta, 2013). Due to complexity of contamination movement in the groundwater and the large scale of the contaminated sites, data collecting can be very difficult and costly. Therefore, it is vital to optimally design monitoring networks. There is still a gap between previous design approaches and the accuracy in identification of contamination source release histories using contaminant observation data. Therefore, this paper focuses on a monitoring network design approach dedicated to reducing uncertainty in recovered release histories and budgetary constraints.

METHOD

The contaminant release histories are generally identified by minimizing the differences between the estimates and the actual observed contaminant concentrations collected at monitoring wells (Amirabdollahian & Datta, 2014). In this paper, it was assumed that a set of possible estimates of contaminant release histories were available. The proposed design method consisted of a two-objective optimisation algorithm.

$$OBJ1 = Max \sum_{i=1}^{N} X_i \left(\sqrt{\sum_{j=1}^{P} \left(Cest_{i,k}^{j} - Cest_{i,k}^{ave} \right)^2 / (p-1)} \right) \qquad OBJ2 = Max \sum_{i=1}^{N} \sum_{j=1}^{P} X_i \times Cest_{i,k}^{j} \tag{1}$$

$$Cest_{i,k}^{j} = f(D, q_j) \quad j = 1,\ldots,\mathrm{P}; \quad i = 1,\ldots,\mathrm{N} \qquad \sum_{i=1}^{N} X_i \le Max(M) \tag{2}$$

where N and P are the number of candidate monitoring locations and the available possible set of contaminant release histories. $Cest_{i,k}^{j}$ is the estimated concentration at monitoring location i and time k estimated using jth possible contamination source release history. $Cest_{i,k}^{ave}$ is estimated concentration at monitoring location i and time k, averaged over all possible set of source release histories. X_i is the decision variable which is a flag which is one when the candidate monitoring well location i is selected, otherwise it is zero. The two objective functions are given in (1). The first one is aimed at selecting monitoring locations which can capture more uncertainty. The Second one is aimed at finding locations where the estimated concentrations are large. Constraints are shown in (2). The first constraint represents the flow and transport simulation models externally linked to the optimisation algorithm. D is the aquifer hydrogeological parameter values. q_j is the jth set of possible source contaminant release history. In the second constraint, Max(M) is the maximum number of monitoring locations. The groundwater contaminant transport simulation model was MT3DMS (Zheng & Wang, 1999). The solutions of the two-objective system were obtained using Non-dominated Sorting Genetic Algorithm (NSGA-II).

RESULTS AND DISCUSSION

The performance of the proposed methodology was evaluated for an illustrative 3-D contaminated study area measuring 3350m × 2490m × 60m (Fig. 1). Two water extraction wells, two active and one inactive point sources (shown by filled circles, and △ in Fig. 1, respectively), and landfill (distributed contamination source) were included in the model. The

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existing monitoring locations are showed by numbers in Fig. 1. The study period is 10 years divided into five equal length stress periods of two years each. All sources were considered as active in the first four stress periods. The contaminant concentration monitoring data were collected every six months. Using 8 years of monitoring data, the initial estimations of contaminant release histories were found. 50 (= P) possible set of release histories had been identified. However, among these 50, one set had to be selected as the most probable. Therefore, new monitoring locations were selected using the proposed methodology. 20 (= N) locations are specified as candidate locations for the new monitoring wells. Max(M) is 5. The new selected monitoring locations are shown by ○ in Fig. 1. The contaminant concentrations at these 5 points, in addition to the pre-existing 13 locations, were measured after 8.5 and 9 years of pollutant injection. Then all the observation data were used to estimate source release histories using Amirabdollahian and Datta (2014) source identification method. Another 50 possible contaminant release histories were estimated. Fig. 2 shows the actual and the average initial possible injection fluxes and the average estimated source injection fluxes after utilizing the new selected monitoring locations in the source identification algorithm. It is demonstrated that the estimated fluxes for the decision variables 5-13 has improved and are closer to the actual values. Therefore, the new monitoring network has contributed substantially to improve the accuracy in recovering the unknown source release history.

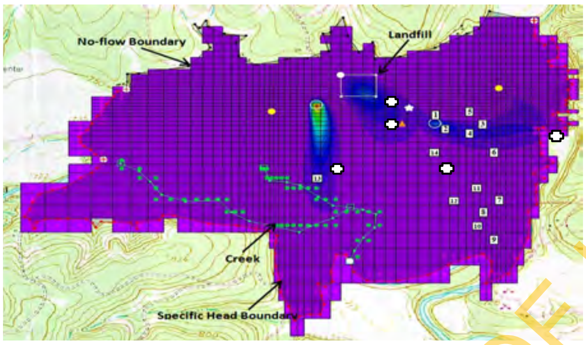

Fig. 1. The study area

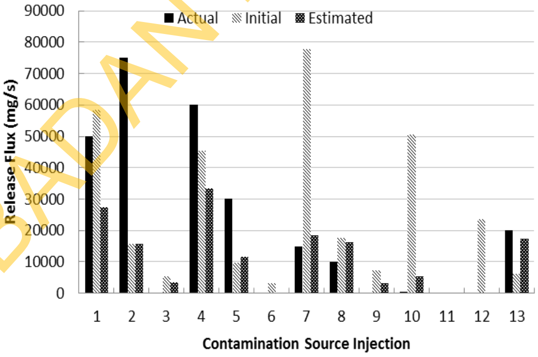

Fig. 2. Source contaminant injection history.

CONCLUSIONS

This paper focused on the design of monitoring network dedicated to decrease uncertainty in the unknown recovery of contamination injection history at sources. The two-objective design method aimed to select monitoring locations which would decrease uncertainty in the contaminant source release history estimation and capture large contaminant concentration values. Using an illustrative contaminated study area, it was demonstrated that the proposed methodology substantially contributes to increase the accuracy in recovering the source injection histories. At the end, the authors acknowledge the financial support for this work provided by CRC-CARE (Project No. 5.6.03.09/10 (2.6.03), B. Datta), and James Cook University, Australia.

REFERENCES

Amirabdollahian, M., & Datta, B. (2013). Identification of contaminant source characteristics and monitoring network design in groundwater aquifers: an overview. *Journal of Environmental Protection, 4*(5A), 26-41.

Amirabdollahian, M., & Datta, B. (2014). Identification of Pollutant Source Characteristics under Uncertainty in Contaminated Water Resources systems using Adaptive Simulated Anealing and Fuzzy Logic. *International Journal of GEOMATE, 6*(1), 757-762.

Zheng, C., & Wang, P. P. (1999). A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems *Documentation and User's*. Citeseer.

P4

HEAD IN THE CLOUD: MOBILE COMPUTING TRANSFORMING THE DELIVERY OF MULTI-SITE INVESTIGATIONS

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INTRODUCTION

Recent advances in technology associated with mobile computing, telecommunication networks and cloud servers has stimulated the spread of pervasive multimedia applications into the field of contaminated land assessment. The combination of these technologies has transformed the design and execution of multi-site linear projects in Australia through cloud based collection, processing, analysis and disseminating site investigation data.

The following discussion will outline the benefits and efficiencies realised through the application of these technologies.

DISCUSSION

The combination of technologies were selected to deliver a multi-site linear project in Australia. The soil inspection and sampling program was completed across four states over a two-month period, with hundreds of individual inspections conducted by 15 different staff. The adopted technologies included:

(a) mobile devices (Android and IOS devices with inbuilt camera and GPS),
(b) customised mobile application for online and offline data collection (ArcGIS Collector),
(c) data connection (4G or 3G),
(d) cloud server accounts (Amazon Web Service and ArcGIS Online), and
(e) office data management system for handling and accessing spatial data (ESRI Geodatabses, SQL database).

This approach was selected due to the availability of low cost cloud computing solutions, which provided similar opportunities across many sectors involved in data collection tasks. Cloud computing involves information being stored in large-scale data centres all over the world and temporarily accessed by users (Chen 2014). The key opportunity that cloud computing offered to the project was the ability to deliver scalable IT-enabled data, software, and hardware capabilities as a service (Chen 2014). This approach provided a paradigm shift away from traditional expectations and approaches to the collection of site data.

The traditional linear approach to the collection of site data (Fig. 1) can be sufficient on a small single project, however it lacks the ability to create value or improve quality across a large multi-site project due to each task being planned and undertaken in a stepwise fashion without considering the information life-cycle. For cloud computing and mobile technologies to be adequately applied to contaminated site assessments, the data management life-cycle for the entire project needs to be mapped out to understand the multiple data connections between each task (Fig. 2).

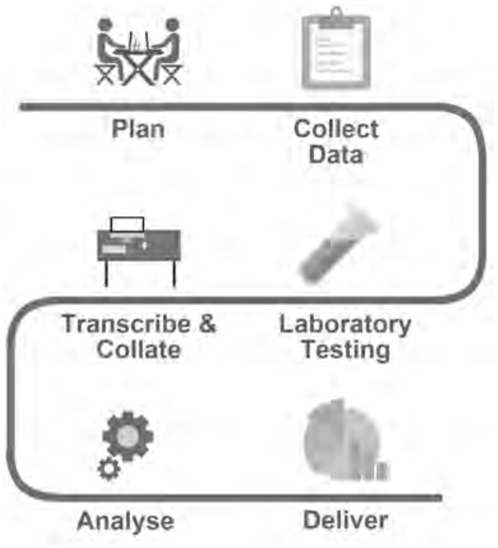

Fig. 1. Traditional linear approach to the collection of site data.

Fig.2. Integrated approach to the collection of site data.

The benefits of adopting the aforementioned technologies within an integrated data management approach were not simply associated with collecting information in an electronic format. The benefits also extend to the ability for multiple teams across multiple sites to access, collect and review information simultaneously using a single dataset, while office based staff were able to track progress and review records as they were collected. The main efficiency gains and quality improvements that were achieved were associated with the data collection, collation, and analysis stages.

The project data model (schema) was defined at the beginning of the project to ensure that the clients objectives would be met. The schema was defined by mapping out the information that was required for each site, then categorising these details into specific attributes. An ArcGIS Collector application was created with a geodatabase that mirrored the project data schema, with domains setup as pre-defined drop-down menus to simplify the data entry process, and to standardise the site descriptions. The mobile application also facilitated the ability for multiple photographs to be attached to any site observation.

The success of the approach was validated by the following achievements:

- The ability to provide automated status updates outlining the exact number of inspections conducted, samples collected, and summary statistics for observations.
- Time and quality improvements associated with the preparation of daily chain of custody documentation.
- The ability for autonomous field staff to have access to the same dataset, providing the ability to see each other's progress in a map based system (this also ensured that sites weren't accidently re-sampled).
- Photographs attached to inspection records allowed office based staff to provide interpretation and live support for field staff with any queries.

REFERENCES

Chen, M., Yulei, W., and Vasilakos, A.V. (2014) Advances in Mobile Cloud Computing. *Mobile Networks and Applications* 19.2: 131-132.

SIMULATION OF COMPLEX GEOCHEMICAL PROCESSES IN CONTAMINATED AQUIFER SITES USING SURROGATE MODELS AS APPROXIMATE SIMULATORS

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INTRODUCTION

Reactive transport processes of AMD, in contaminated groundwater system, especially with multiple species, is a complex and highly non-linear process. Simulation of such complex geochemical processes using efficient numerical models is generally computationally intensive. In many contaminated groundwater aquifer management scenarios, an efficient strategy is necessary for effective and reliable remediation and control of the contaminated aquifer. Also, in a hydrogeologically complex aquifer site e.g., mining site, acid mine drainage (AMD) and the reactive chemical species together with very complex geology complicates the characterization of contamination source location and pathways.

In such contamination cases, it becomes necessary to develop optimal source characterization models, and strategies for future remediation. Solution of optimization models either for source characterization or optimal management strategy development requires the incorporation of the complex physical processes in the aquifer (Sreekanth & Datta, 2011). Also, most of the developed optimization models for source characterization or remediation strategy development require repeated solution of the numerical simulation models within the optimization algorithm. This process is enormously time consuming and often restricts the computational feasibility of such optimization approaches (Sreekanth & Datta, 2011).

In order to overcome these computational restrictions, and to ensure computational feasibility of characterizing sources and pathways of contamination it is computationally advantageous to develop surrogate models which can be trained using solutions obtained from rigorous numerical simulation models. Trained and tested ensemble Genetic Programming (GP) models are developed as robust surrogate models, using the simulated response of a complex contaminated aquifer to randomly generated source fluxes (Datta et al., 2013). Performance of GP models are evaluated by comparing GP model solutions with solution results obtained by using a rigorous numerical simulator, HYDROGEOCHEM 5.0 [HGCH] (Sun, 2004), to simulate flow and transport processes for a study area resembling an abandoned mine site incorporating acid mine drainage. Therefore, this study develops ensemble GP models to approximately simulate 3-dimensional, reactive, multiple chemical species transport in contaminated aquifers.

METHODS

The methodology developed includes two main components. In the first step, the simulation model for the flow and transport processes is described, and complex chemical reactive transport process is simulated by the HGCH, a 3-dimensional coupled physical and chemical transport simulator, to realize the reactive contaminants behaviours in contaminated aquifers. The hydrogeochemical data and boundary conditions at the illustrative study site are similar to an abandoned mine site in Queensland, Australia. Trained ensemble GP based surrogate models are then developed to approximately obtain concentrations of the chemical contaminants at different times in specified locations while incorporating uncertainties in hydrogeological aquifer parameters like hydraulic conductivity. Comparison of the spatio-temporal concentrations obtained as solution by solving the implemented numerical three dimensional reactive contaminant transport simulation model (HGCH) and those obtained using ensemble GP models are then presented to demonstrate the potential applicability and the efficiency of using GP ensemble surrogate models under aquifer uncertainties. In order to evaluate the performance of the proposed methodology, ensemble GP based surrogate models are utilized for an illustrative study area. The specified hydrogeologic conditions resemble a homogeneous and isotropic aquifer.

RESULTS AND DISCUSSION

The numerical simulation output obtained using HGCH are compared with the results obtained using developed ensemble genetic programming based surrogate models at the observation wells Figure 1(a) illustrates these comparison results. Each well is marked on the x-axis and each of the bars corresponds to contaminant concentration in each well, obtained by HGCH and ensemble GP models. Figure 1 shows that the results obtained from ensemble GP models are very close to the simulated results obtained using a numerical simulation model, and also incorporates uncertainties. Figure 1 (b) shows the summation of normalized error at each of the observation locations in network monitoring. As expected, the ensemble GP models provide relatively accurate results for concentration at observation locations incorporating complex contaminant transport processes under uncertainties. The benefit of using developed GP models is that the solution results can be obtained in typically fraction of a second, and do not requires long computational time unlike the complex numerical simulation models. The numerical results obtained for this mine site aquifer with complex transport processes using HGCH simulation model after several hours. Especially, this computational time saving could be critical in development and solution of linked simulation- optimization models (Datta et al., 2013) for developing remediation strategies for contaminant aquifer management.

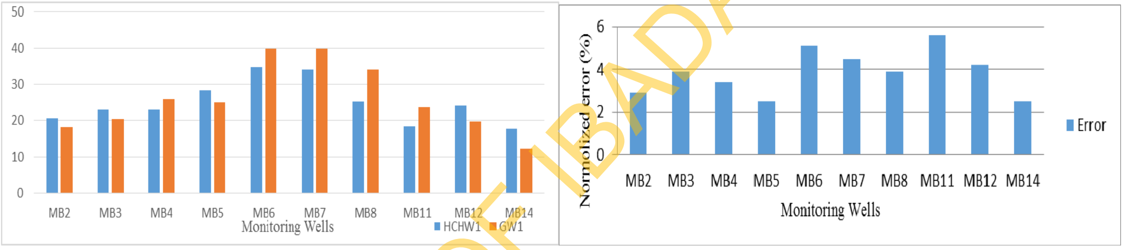

Fig. 1. (a) Comparison data for pollution concentration and (b) normalized error in observation wells

CONCLUSIONS

The Genetic Programming based surrogate models performed satisfactorily and show the potential for use of GP based surrogate models to simulate complex geochemical processes in the aquifer. Then trained and tested surrogate models can ensure the computational feasibility of optimization based models for source characterization, and can help in the development of optimum strategies for the ultimate remediation of such contaminated aquifers. This study demonstrated the utility and feasibility of using trained and tested GP models and ensemble GP models as a tool for approximate simulation of the complex geochemical processes in a contaminated aquifer sites like mine sites.

REFERENCES

Sreekanth, J., Datta, B. (2011) Comparative Evaluation of Genetic Programming and Neural Network as Potential Surrogate Models for Coastal AquiferManagement Water Resour Manage (25): p. 18.

Datta, B., Prakash, O., Campbell, S., Escalada, G. (2013) Efficient Identification of Unknown Groundwater Pollution Sources Using Linked Simulation-Optimization Incorporating Monitoring Location Impact Factor and Frequency Factor. Water Resour Manage. 27: p. 18.

Sun, J. (2004) A Three-Dimensional Model of Fluid Flow, Thermal Transport, and Hydrogeochemical Transport through Variably Saturated Conditions. . M. S. Thesis. Department of Civil and Environmental Engineering, University of Central Florida, Orlando, FL 32816.

WEB BASED GUIDANCE FOR UNDERSTANDING BIOCHEMICAL REACTORS FOR THE TREATMENT OF MINING INFLUENCED WATER

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INTRODUCTION

The Interstate Technology Regulatory Council is a state-led, national coalition of industry, governmental agencies, and community stakeholders within the United States dedicated to help interested parties achieve a better understanding of environmental protection through the use of innovative technologies. Through open communication among its partners, ITRC is streamlining and standardizing the regulatory review process for better, more cost-effective, environmental technologies. Funding comes from the Departments of Defense and Energy, the US Environmental Protection Agency as well as industry and is used to support teams to address state environmental priorities. These teams research, develop, and present guidance on the use of technologies to address major environmental problems facing the states. One of the teams was organized to review various technologies to address the use of biochemical reactors for the treatment of mining influenced water.

The ITRC Mine Waste Team was formed in 2008 to address mine impacted solids and water. This Team produced a web-based guidance to help select technologies that address a wide variety of mine waste issues (ITRC MW-1, 2010 at http://www.itrcweb.org/miningwaste-guidance). During the development of the original guidance, the team felt that more information on the design, use and success of biochemical reactors (BCRs) was needed. As a result, in 2013, the team completed a web-based guidance on the use of BCRs. (http://itrcweb.org/bcr-1/). The guidance contains information on the applicability, design, construction, monitoring and maintenance of BCRs as well as discussions on the related regulatory and public stakeholder issues. Fifteen case studies are included.

BCRs use a combination of biological and chemical reactions to transform minerals and metals in mine water in semi-passive systems. BCRs are engineered treatment systems that use an organic substrate to promote microbial and chemical reactions to transform metals and minerals in the system to reduce concentrations of metals, acidity, and sulfate in mining-influenced waters (MIWs). While this chemistry has been described in detail and is fairly well understood, much has been learned over the past 20 years on how to improve the effectiveness, permeability, and longevity of these systems. In addition to the guidance, the ITRC BCR Team developed a training program to help interested parties understand how to use this guidance and apply its concepts to their particular needs.

METHODS

The guidance contains an in-depth analysis and overview of BCR applicability and design, including a decision tree and section on testing, design, construction, and monitoring considerations. The overview presents the current understanding of what is typically considered a BCR, what microbial and chemical processes are involved with their operation, and what types of applications are most appropriate for the current generation of systems. The testing section presents a general approach to collect sufficient information to begin

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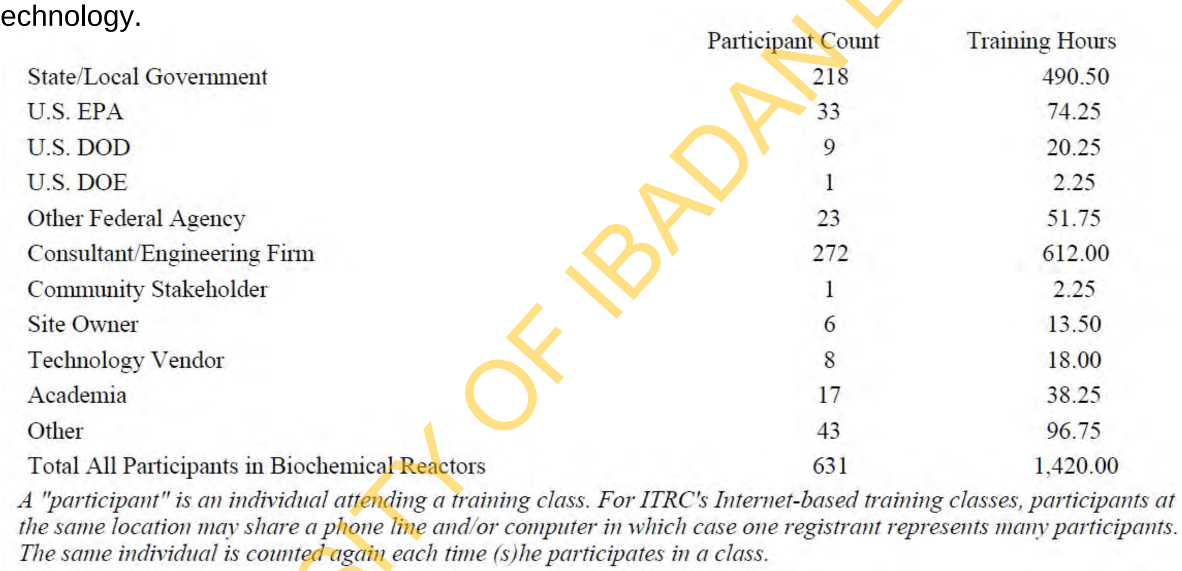
design. This includes a brief discussion of various differences in designing BCRs for simple systems with relatively neutral pH water and predominantly dissolved iron and manganese to complex hard rock mine systems involving complex acid chemistries as well as neutral to net alkaline chemistries. Although not intended to be a design document, the design section includes a discussion of the evolution of BCRs, typical design components and considerations, hydraulics, site control and typical submittals. The construction section presents information on typical construction issues including physical setting, BCR construction elements, system performance, site restoration, and site security.

RESULTS AND DISCUSSION

The guidance is available, free of charge, to anyone with access to the internet. In addition to the guidance the ITRC Mining Waste Team organized, developed, and conducted classes through an internet training program to assist interested parties in learning how to use the guidance. Since November 2013, over 790 individuals participated in the BCR Team training program. This included participants form state and local government, U.S. EPA, U.S. Department of Defense, U.S. Department of Energy, consulting and private engineering firms, community stakeholders, site owners, technology vendors, and academia. Figure 1 presents a breakdown of participants from November 2013 through December 2014. The presentation will introduce the guidance and introduce some of the highlights of the technology.



	Participant Count	Training Hours
State/Local Government	218	490.50
U.S. EPA	33	74.25
U.S. DOD	9	20.25
U.S. DOE	1	2.25
Other Federal Agency	23	51.75
Consultant/Engineering Firm	272	612.00
Community Stakeholder	1	2.25
Site Owner	6	13.50
Technology Vendor	8	18.00
Academia	17	38.25
Other	43	96.75
Total All Participants in Biochemical Reactors	631	1,420.00

A "participant" is an individual attending a training class. For ITRC's Internet-based training classes, participants at the same location may share a phone line and/or computer in which case one registrant represents many participants. The same individual is counted again each time (s)he participates in a class.

Figure 1 ITRC BCR Training Program Participants November 2013 – December 2014

CONCLUSIONS

Mining is essential to the economy of the United States, but historical mining practices and some current practices has led to the discharge of environmentally detrimental mining influenced water. These waters typically contain high concentrations of metals and can contain high levels of acidity. Traditional water treatment processes can be effective on these waters but due to their expense, especially at remote sites, are not an attractive alternative. BCRs can be effective as semi-passive systems for many of these sites. ITRC has developed a successful web-based program to assist regulators, practitioners, industry, and stakeholders better understand the applicability of biochemical reactor systems.

REFERENCES

Biochemical Reactors for Treating Mining-Influenced Water, November, 2013, ITRC, Sponsored by Environmental Council of the States, Washington, D.C., Available from: http://itrcweb.org/bcr-1/. [16 July 2015]

Mining Waste Treatment Technology Selection, 2010, ITRC, Sponsored by Environmental Council of the States, Washington, D.C., Available from: http://www.itrcweb.org/miningwaste-guidance/. [16 July 2015]

P7

A SIMPLE DETERMINATION METHOD FOR MULTIPLE PFCS IN WATER AND SOIL MEDIA THROUGH LC-MS SINGLE QUADRUPOLE TECHNIQUE

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INTRODUCTION

Aqueous film forming foam (AFFF) formulations are used to extinguish hydrocarbon-fuel fires in particular and contain per- and polyfluorinated alkyl surfactants. These have been reported to accumulate in the environment as persistent organic pollutants (POPs). Research focus has increased in recent years in identifying and quantifying such compounds. As also there is a constant demand from regulatory bodies to monitor emerging perfluorochemicals (PFCs).

However, many challenges exist for the accurate analysis of PFCs. Contamination from any PTFE parts easily leads to blank signals. This includes the HPLC system itself, from solvent lids, cap liners, etc. Sample matrix interferences could lead to ionisation suppression or enhancement. PFCs solubility decreases significantly with increased salt content. pH affects solubility and ionisation.

METHODS

In this study, a liquid chromatography-mass spectrometry (LC-MS) single quadrupole method was developed for the simultaneous determination of a mixture of PFCs comprising 5 perfluoroalkyl carboxylic acids (PFCAs), 4 perfluoroalkyl sulphonates (PFASs) and a perfluoroalkyl sulphonamide (PFSA) commonly found in contaminated sites (soil and water). The target PFCs included C4 - C12 analogues. Complete separation of all surfactants was achieved using a RP-C18 (4.6X100mm, 3.5µm) column with aqueous ammonium acetate (5mM, pH=6.5) and methanol gradient elution under optimal conditions (Fig.1).

RESULTS AND DISCUSSION

The recovery of 10 mixed standards was 98 - 116%. The method was applied successfully to samples (see Table 1). Detection limits were not pursued below 1 µg/L.

The use of strong ion exchange column (Agilent Bio SAX, NP5, SS) and guard column C18 (SB-AQ) prior to injections reduces interferences

CONCLUSIONS

A simple analytical method was developed for simultaneous measurement of PFCs employing single quadrupole LC-MS system. This method was successfully applied to water and soil samples from various contaminated sites. pH and presence of salt caused matrix effects and should be considered in analyses.

REFERENCES

Place, B. J. and Field, J.A. (2012) Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Enviro. Sci. Technol.* 46, 7120-7127.
ISO 25101
US EPA SW846

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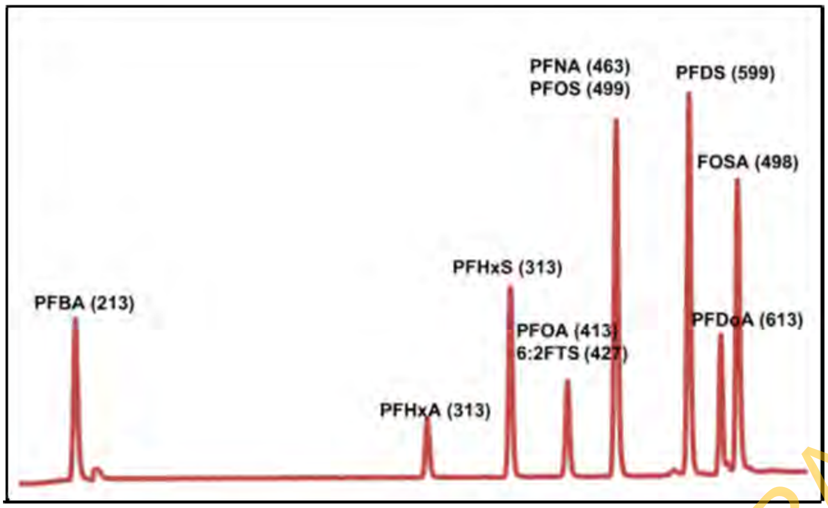

(These compounds in the two overlapped peaks can be discriminated from their masses extracted from SIM mode)

Fig. 1. Chromatogram of 50 μg/L standard solution of 10 PFCs (ESI, SIM, negative mode)

Table 1. Site samples result (Units: μg/L in water, μg/kg in soil)

Sample	PFBA	PFHxA	PFHxS	PFOA	6:2FtS	PFOS	PFNA	PFDS	PFDoA	FOSA
Soil 1	<LOR	<LOR	<LOR	<LOR	<LOR	18.5	<LOR	<LOR	<LOR	<LOR
Soil 2	<LOR	<LOR	<LOR	<LOR	<LOR	40.3	<LOR	<LOR	<LOR	<LOR
Soil 3	4.0	7.9	8.4	5.0	37.8	69.5	9.5	<LOR	<LOR	<LOR
Soil 4	<LOR	<LOR	4.1	3.3	<LOR	5.1	<LOR	<LOR	<LOR	<LOR
Soil 5	<LOR	<LOR	<LOR	<LOR	<LOR	53.7	<LOR	<LOR	<LOR	<LOR
Water (RO)	9.5	15.6	28.5	8.9	<LOR	23.3	<LOR	<LOR	<LOR	<LOR
Water (pound)	950	1440	3590	960	150	6120	<LOR	<LOR	<LOR	<LOR

ADSORPTION OF PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOIC ACID (PFOA) BY AN ORGANICALLY MODIFIED PALYGORSKITE

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INTRODUCTION

Despite previous research focused on the global distribution, long-term fate and the bioaccumulation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), knowledge related to the development of different remediation options is largely lacking for these compounds (Kupryianchyk et al. in press). Clay minerals including fibrous palygorskite have a number of potential applications in the treatment of emerging environmental contaminants. One novel approach for improving the contaminant-removal efficiency of clay minerals has been the development of organoclays which significantly add to the remediation performance of the material. Similar to lamellar clay minerals, palygorskite can also serve as an effective host of organic surfactants. However, information on removal performance of contaminants having emerging concerns (e.g., perfluorooctane sulfonate and perfluorooctanoic acid) by organopalygorskite is scarce in the literature.

The aim of this study is to assess the adsorption of PFOS and PFOA by an organically modified palygorskite under environmental conditions.

METHODS

The palygorskite (Grade 050F) used in this study originated in Western Australia and was purchased from Hudson Resources Ltd. (Australia). This palygorskite was modified with dimethyldioctadecylammonium bromide (DMDOA) (Sigma-Aldrich, Australia) at a rate equivalent to 200% CEC of the clay mineral. The mixture (10:1 ratio) was stirred gently on a 70ºC water bath for 5 hours. At completion of the reaction, the modified palygorskite was separated from the aqueous phase through centrifugation at 4000 rpm for 15 min (Multifuge 3 S-R, Hevaeus, Kendro Instruments Australia Pty. Ltd., Australia). The product was washed repeatedly with copious amount of distilled water until the decanted aqueous phase provided negative test for bromide with $AgNO_3$. The cation exchange capacity (CEC) of this organopalygorskite was 17 cmol (p^+)/kg and the BET specific surface area was 24.3 m^2/g.

The adsorption of PFOS and PFOA onto the organopalygorskite was evaluated by the batch method. Adsorption isotherms at two different temperatures (20 and 37ºC) were obtained by equilibrating the adsorbent with constant volume of adsorbate solutions (40 mL) at PFOS and PFOA concentrations ranging from 0 to 100 mg/L. The mixture was agitated for 4 hours using an end-over-end shaker (sufficient time to reach equilibrium). The adsorption kinetic experiments were conducted at 22ºC by equilibrating the adsorbent with100 mL of known concentration solutions of the adsorbates (74 mg/L for PFOS and 34 mg/L for PFOA) for various time intervals. All the experiments were carried out in duplicate and average values were recorded and control experiments in the absence of adsorbent material showed no adsorption of PFOS and PFOA onto the laboratory ware.

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RESULTS AND DISCUSION

The adsorption data fitted well to Freundlich isothermal ($R^2 \geq 0.8$) model and pseudo-second order kinetic model as shown in Figure 1.

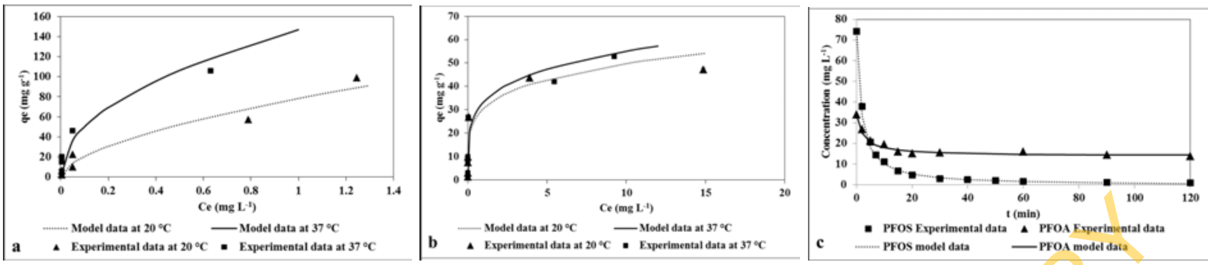

Figure 1. Adsorption isotherms for a) PFOS @ b)PFOA c) Kinetics data

Fitting of the adsorption data to Freundlich model implied that the bonding energy of the adsorbates on the heterogeneous organopalygorskite surface decreased with fractional coverage of the surface area (Sarkar et al., 2011; Das et al., 2013). In addition, high K values (33.3>mg$^{1-\beta}$ g^{-1} L$^{\beta}$) indicated that the organopalygorskite had a high adsorption capacity for PFOS and PFOA.

Effect of temperature on the adsorption of PFOS and PFOA by the modified palygorskite was studied at 20 and 37ºC, representing the average maximum temperatures encountered in Australia during warmer season. The K value was much higher at 37ºC than 20ºC for PFOS adsorption (146 and 78 mg$^{1-\beta}$ g^{-1} L$^{\beta}$, respectively) and slightly higher for PFOA adsorption at higher temperature (33 mg$^{1-\beta}$ g^{-1} L$^{\beta}$ and 30.6 mg$^{1-\beta}$ g^{-1} L$^{\beta}$ for 37°C and 20°C, respectively). It indicated that the adsorption reaction was endothermic in nature. In addition, the n values ($n \geq 1.7$) indicated a highly favourable adsorption process at this temperature range.
The kinetic data (Fig. 1c) indicated a very fast kinetics where most of the adsorption occurred during the first 20 minutes for both PFOS and PFOA and the equilibrium reached after only 120 minutes.

CONCLUSIONS

A palygorskite based organoclay was developed to remove PFOS and PFOA from water. The organopalygorskite displayed high adsorption capacity for PFOS and PFOA and fast kinetics (2 hours to reach equilibrium). An increase in temperature enhanced the adsorption capacity due to endothermic nature of the adsorption process. The findings of this study indicate that the organopalygorskite has great potential for remediation of PFOS and PFOA contaminated water.

AKNOWLEDGEMENTS

This research was funded by the Department of Defence, Australian Government, through CRC CARE. Support from Dr. Wei Hong Wang in HPLC analysis of PFOS and PFOA and infrastructural support given by the Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia is gratefully acknowledged.

REFERENCES

Das, P., Arias E, V., Kambala, V., Mallavarapu, M., and Naidu, R. (2013). Remediation of perfluorooctane sulfonate in contaminated soils by modified clay adsorbent—a risk based approach. *Water Air Soil Pollut*. 224, 1-14.

Kupryianchyk, D., Hale, S.E., Breedveld, G.D., and Cornelissen, G., In press. Treatment of sites contaminated with perfluorinated compounds using biochar amendment. Chemosphere doi:10.1016/j.chemosphere.2015.04.085.

Sarkar, B., Megharaj, M., Xi, Y., and Naidu, R. (2011). Structural characterisation of Arquad® 2HT-75 organobentonites: Surface charge characteristics and environmental application. J. Hazard. Mater. 195, 155-161.

ENVIRONMENTAL IMPACTS OF AQUEOUS FIRE FIGHTING FOAMS — AN OVERVIEW

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INTRODUCTION

Aqueous fire fighting foams (AFFF) are water based foams used for suppression of hydrocarbon fires frequently containing surfactants such as sodium alkyl sulfate and fluorosurfactants such as fluorotelomers, perfluorooctanoic acid (PFOA) or perfluorooctanesulfonic acid (PFOS). AFFFs have undesirable environmental impacts on the account of the fluorosurfactants used in their formulations. Among these, PFOS and PFOA were found to be extremely persistent in the environment and bioaccumulate in living organisms even from the Arctic (Wang et al., 2009). PFOS and PFOA appear to possess toxicity, has endocrine disrupting activity, and carcinogenicity (Beach et al., 2006). Efforts were underway to identify and develop more environmentally safer firefighting chemicals. Continuous research has led to the development of AFFFs which do not include PFOS as the fire fighting active ingredient. However, the manufacturers do not list the chemical composition of the newly formulated foams enabling much difficulty in the assessment of the environmental impact that could be caused.

CLASSIFICATION OF AFFF PRODUCTS

AFFFs may be classified on the basis of the type of fluorosurfactants in it. One class based on PFOS and structurally related compounds are prepared by direct electrochemical fluorination. A much safer substitute is the use of protein foams which unlike the AFFFs are biodegradable in nature (Wikipedia accessed on 1.05.2015). A further improvement to the performance efficiency of AFFFs is the invention of alcohol-resistant aqueous AFFFs. The chemistry of AR-AFFF is similar to that of AFFFs in terms of the presence of fluorinated surfactants, additionally they also contain synthetic polymers (polysaccharide polymer). Such polymer allow the foam to form a layer that encases it from the fuel thus resulting in their application to fires even where the fuel is miscible with water (e.g. alcohols) (Manzello and Yang, 2002).

PERSISTENCE, BIOACCUMULATION AND TOXICITY

The widespread use and injudicious release of AFFFs have resulted in their easy entry in the oceans and penetration to the groundwater. PFOS and PFOA existing in AFFFs have been found to be extremely persistent in the environment (Fromme et al., 2009). PFOS anion is resistant to photolysis, hydrolysis and biodegradation with a half-life value of ≥ 41 years (Beach et al., 2006). Because of their resistance to breakdown reactions they can also travel for longer distances before being re-deposited. Hence, PFOS and PFOA are found to be globally distributed with PFOS at a higher concentration than PFOA (Wang et al., 2009).

PFOS occurring in most AFFF formulations was found to exhibit low to moderate acute toxicity. The adverse effects included reduction in body weight, enlargement of liver, hepatotoxicity, decreased serum cholesterol levels, teratogenecity, neurotoxicity, induced perioxisome proliferation and endocrine disruption (Lau et al., 2007). Some human studies could find a possible correlation between PFOS levels and natal factors such as birth weight (Olsen et al., 2009). PFOA the other common active ingredient of AFFFs causes developmental toxicity (Rosen et al., 2009). The US EPA classified PFOA as a likely human carcinogen.

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REMEDIAL OPTIONS

The application of conventional treatments for removing anionic perfluorinated surfactants present in AFFF formulations from aqueous bodies or soil matrices are restricted by technical and/or economical constraints. Perfluorinated surfactants are also not amenable to biological treatments due to their outstanding stability against microbial attack. The techniques that are considered as potential treatment options include membrane processes, decomposition by chemical approaches involving high-temperature, sonochemical treatments (Vecitis et al., 2009), and reduction with zero-valent iron in subcritical water (Lee et al., 2009).These treatment options have some limitations mainly because of their high energy requirement and/or interference by other compounds present in the contaminated site. Adsorption to various matrices such as granular activated carbon, polymer adsorbents, naturally modified zeolites (varying in Si/Al ratios) or sludges are other viable low-cost alternatives for the removal of AFFF compounds (Ochoa-Herrera and Sierra-Alvarez, 2008).

CONCLUSION

Hydrocarbon fuel fires posing a serious threat to life and property could be managed with AFFFs which are complex mixtures of fluorocarbons and hydrocarbon based surfactants. Fluorosurfactants like PFOS and PFOA occurring in AFFFs have been found to be extremely persistent, moderately bioaccumulative and even toxic to a certain extent. Cheap remedial options of contaminated sites could be achieved by adsorbing on naturally modified clays. However, the performances of the treatment options were not very consistent with respect to desired efficiency level.

REFERENCES

Beach, S.A., Newsted, J.L., Coady, K., Giesy, J.P., 2006. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). Reviews of Environmental contamination and Toxicology 186,133-174.

Ochoa-Herrera, V., Sierra-alvarez, R., 2008. Removal of perfluorinated surfactants by sorption into granular activated carbon, zeolite and sludge. Chemosphere 72, 1588-1593.

Wang, T., Wang, Y., Liao C., Cai, Y., Jiang, G., 2009. Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm Convention on persistent organic pollutants. Environmental Science and Technology 43, 5171-5175.

Fromme, H., Tittlemier, S.A., Völkel, W., Wilhelm, M., Twardella, D., 2009. Perfluorinated compounds – Exposure assessment for the general population in western countries. International Journal of Hygiene and Environmental Health 212, 239-270.

Rosen, M.B., Wolf, D.C., Abbott, B.D., Corton, J.C., Schmid, J.E., Wood, C.R., Das, K.P., Zehr, r.D., Lau, C., 2009. Developmental toxicogenomic studies of PFOA and PFOS in mice. Reproductive Toxicology 27, 409-416.

Olsen, G.W., Butenhoff, J.L., Zobel, L.R., 2009. Perfluoroalkyl chemicals and human fetal development: An epidemiologic review with clinical and toxicological perspectives. Reproductive Toxicology 27, 212-230.

Manzello, S.L., Yang, J.C., 2002.The effect of an alcohol resistant aqueous film forming foam (AR-AFFF) on the evaporation, boiling, and collision dynamics of a water droplet on a heated solid surface. Journal of Colloid and Interface science 256, 418-427.

Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicological Sciences 99, 366-394.

PHYTOTOXICITY OF BUSH FIREFIGHTING FOAMS

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INTRODUCTION

Bush firefighting foam products are used as effective and efficient agents for suppressing fire ignited by ordinary combustible materials. They form thick and dense foam which acts as a blanket on the fire and they are mainly used for combating Australian wildfires. It negates oxygen to the fire which results in smothering fire and absorbing radiant heat, thus preventing sources of the fire from reaching dangerously hot temperatures. The class A bush firefighting foams includes, Fire-Brake™3150A and Phos-Chek® WD 881, the fire retardants/suppressants, Phos-Chek® MVP-F and Phos-Chek® Insul 8. Firefighting products containing fluorosurfactants such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are generally considered to cause environmentally toxic due to persistence and bioaccumulative nature (Boudreau et al. 2003; Li, 2009). There is, however, a paucity of research on bush firefighting foams particularly their toxic effects on higher plants. Therefore understanding about the firefighting products is very important in selecting the right product for the purpose.

METHODS

The commercial seed materials were obtained from Bunnings warehouse (Adelaide, SA). The seeds were surface sterilised by rinsing the seeds with 95 % ethanol and then with 10 % hydrogen peroxide and 1.25% sodium hypochlorite. The seeds were immersed completely for 3-5 min in sterilizing solution and rinsed several times with sterile water and air dried. Briefly, two layers of filter paper (Whatman No. 1) was placed into each 90 mm sterile petri plate. Five ml of test solution (0, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0, 7.5,10, 15 and 20 %) of firefighting foams was added to soak filter paper. Seeds were then arranged (10 seeds/ plate) with 1 cm spacing between seeds. Petri dishes were covered and placed in an incubation room (25 ± 2 °C) under dark condition. During incubation, plates were monitored and hydrated with the test solution to prevent the filter papers from drying. After 7 days, the seed germination rate and root length in terms of percentage decrease over control was calculated.

RESULTS AND DISCUSSION

Seed germination and root elongation were the simple, sensitive, cost effective and rapid bioassay used extensively to evaluate acute phytotoxicity of chemicals (Wang et al., 2001). In the present study, phytotoxicity of Class A bush firefighting foams, and fire retardants/suppressants were analysed (Table 1). Based on the initial range finding experiments the test solutions were spiked with Fire-Brake™ 3150A, Phos-Chek® WD 881 and Phos-Chek® MVP-F at concentrations ranging from 0.1 to 10%. Whereas, Phos-Chek® Insul-8 was tested with concentrations ranging from 0.1 – 20% respectively. A dose dependent reduction in germination, root length and shoot length was recorded in both firefighting products.

Zhao et al., (2011) observed a significant reduction in germination and root length was observed in *Brassica chinensis* in six different soils when exposed to PFOS and PFOA at concentrations ranging from 95 to >200 mg kg^{-1} and from 107 to 246 mg kg^{-1}. Similarly, in the present study a significant reduction in seed germination, root and shoot length was observed in Class A firefighting foams, Fire-Brake™ 3150A and Phos-Chek® WD 881 with half maximal effective concentration (EC_{50}) value ranging from 0.26 – 1.18% and 0.06 – 0.52%, respectively. The Phos-Chek® WD881 exhibited higher toxicity on selected plants when compared to Fire-Brake™ 3150A. Fire retardants/suppressants were also found to be phytotoxic to cucumber, maize and onion (Fig.1). The effective concentrations of added Phos-Chek® MVP-F and Phos-Chek® Insul-8 causing 50% inhibition (EC_{50}) in germination, root length and shoot length ranged from 0.8 – 1.7 % and 7.8 – 11.6%, respectively. Cucumber and onion exposed to Phos-Chek® MVP-F recorded high inhibition in germination when compared to maize. Among the four compounds tested, Phos-Chek® INSUL 8 was found to be least toxic to all the plant species tested.

Table 1. Phytotoxicity of bush firefighting foams.

Compounds	Plants	EC_{50} value (% dilution)		
		% inhibition in germination	**% inhibition in shoot length**	**% inhibition in root length**
Fire-Brake™ 3150A	Cucumber	0.97 (0.92 ± 1.04)	0.61 (0.53 ± 0.69)	0.58 (0.53 ± 0.65)
	Maize	1.09 (0.97 ± 1.2)	1.18 (1.05 ± 1.34)	0.94 (0.83 ± 1.11)
	Onion	0.64 (0.58 ± 0.71)	0.45 (0.41 ± 0.53)	0.26 (0.21 ± 0.31)
Phos-Chek® WD881	Cucumber	0.09 (0.08 ± 1.02)	0.06 (0.05 ± 0.07)	0.06 (0.05 ± 0.07)
	Maize	0.36 (0.33 ± 0.39)	0.52 (0.46 ± 0.58)	0.52 (0.46 ± 0.58)
	Onion	0.07 (0.06 ± 0.07)	0.06 (0.05 ± 0.07)	0.06 (0.05 ± 0.06)
Phos-Chek® MVP-F	Cucumber	1.57 (1.45 ± 1.73)	1.07 (0.96 ± 1.22)	0.58 (0.52 ± 0.64)
	Maize	1.41 (1.26 ± 1.58)	1.36 (1.21 ± 1.53)	1.71 (1.62 ± 1.94)
	Onion	0.8 (0.81 ± 1.06)	1.22 (1.07 ± 1.39)	1.64 (1.39 ± 1.92)
Phos-Chek® INSUL-8	Cucumber	8.2 (7.91 ± 8.63)	10.2 (9.63 ± 10.95)	8.65 (8.06 ± 9.29)
	Maize	9.5 (9.14 ± 9.96)	7.89 (7.47 ± 8.12)	5.49 (5.05 ± 5.97)
	Onion	7.8 (7.51 ± 8.32)	11.6 (10.92 ± 12.34)	10.14 (9.46 ± 10.87)

CONCLUSIONS

The phytotoxicity experiment can be used to assess the toxicity of bush firefighting compounds. The onion was found to be more sensitive than other two plant species tested. The phytotoxicity was in the order of Phos-Chek® WD 881 > Fire-Brake™ 3150A > Phos-Chek® MVP-F > Phos-Chek® Insul 8.

REFERENCES

Boudreau, TM, Sibley, PK, Mabury, SA, Muir, DGC & Solomon, KR 2003, 'Laboratory evaluation of the toxicity of perfluorooctane sulfonate (PFOS) on *Selenastrum capricornutum*, *Chlorella vulgaris*, *Lemna gibba*, *Daphnia magna*, and *Daphnia pulicaria*', *Archives of Environmental Contamination & Toxicology*, vol. 44, no. 3, pp. 0307-0313.

Li, MH 2009, 'Toxicity of perfluorooctane sulfonate and perfluorooctanoic acid to plants and aquatic invertebrates', *Environmental Toxicology*, vol. 24, no. 1, pp. 95-101.

Zhao, H, Chen, C, Zhang, X, Chen, J, & Quan, X 2011 'Phytotoxicity of PFOS and PFOA to *Brassica chinensis* in different Chinese soils', *Ecotoxicology and Environmental Safety*, vol. 74, no. 5, 1343-1347.

ACUTE TOXICITY OF
CLASS A FIREFIGHTING PRODUCTS TO ALGAE

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INTRODUCTION

Firefighting formulations are used for the management and suppression of wild fire of grasslands, ranges and forests around the world (Vyas et al. 2009). Firefighting compounds such as Class A (for suppressing fire from wood, paper/organic material), Class B (for suppressing fires from flammable liquids) and fire retardants/suppressants (acts as a structural protectant) are used extensively around the world. Millions of gallons of firefighting compounds are used every year across a wide range of ecosystem comprising undisturbed, environmentally sensitive zones containing fragile flora and fauna (Poulton, 1996).

Class A bush firefighting foams, Fire-Brake™ 3150A and Phos-Chek® WD881 produce thick and dense foam which forms a blanket over fire causing fire to subside. Phos-Chek® MVP-F, a dry concentrate powdered fire retardant salt which is used for wild fire extinguishing disperses through fixed-wing air tankers. Phos-Chek® Insul-8 on the other hand is a fire protection and suppressant gel used as a structural protectant for indirect fire suppression. Firefighting compounds containing fluorosurfactants such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are generally considered toxic causing environmental issues due their persistence and bioaccumulative nature. However, information on the ecotoxicity of non-fluorosurfactant firefighting products is currently very limited. Hence in this study the acute toxicity of Class A firefighting products and fire retardants/suppressants to fresh water, terrestrial and marine algae was investigated.

METHODS

Axenic cultures of *Raphidocelis subcapitata* (freshwater alga), *Chlorella vulgaris* (soil alga) and *Dunaliella tertiolecta* (marine alga) were maintained in OECD, Bold's basal medium and F2 medium, respectively, under continuous illumination at 25 °C in an orbital shaker set at 100 rpm. Based on initial toxicity range finding test, algal acute toxicity tests were conducted using 7 nominal concentrations of firefighting compounds. The test ranged from 0 to 0.1% (Phos-Chek® WD881), 0 to 0.5% (Fire-Brake™ 3150A) and 0 to 1.0% (Phos-Chek® MVP-F & Phos-Chek® Insul-8). Sterile growth medium containing various concentrations of test compounds placed in sterile culture flasks were inoculated with exponentially-growing culture of *R. subcapitata, C. vulgaris* and *D. tertiolecta*. Controls contained only growth medium and algae. The test vessels were incubated in a temperature controlled (25 °C) orbital shaker set at 100 rpm under continuous illumination (200 µE/m2/sec PPFD (Photosynthetic Photon Flux Density)) provided by cool white fluorescent lamps. At the end of 96 hours, the growth of the alga was estimated, in terms of cell count in Neubaur hemocytometer, using a phase contrast microscope (Megharaj et al. 2000). Growth inhibition of the alga served as an endpoint in this bioassay. All the assays were conducted in triplicate. Effective concentration (EC_{50}) was calculated using Probit analysis in Minitab 17.0 statistical software.

RESULTS AND DISCUSSION

In the aquatic ecosystems, algae play a vital role as the benefactor of basic nourishment for food webs and also contributing to the self-purification of polluted water bodies (Ji et al. 2011). Hence assays dealing with the aquatic toxicity utilize alga as a sentinel organism to examine the presence and impact of xenobiotic compounds. In the present study, the toxicity of Class A firefighting foams and fire retardants/suppressants to *R. subcapitata*, *C. vulgaris* and *D. tertiolecta* was examined. The results showed that Class A firefighting compound, Phos-Chek® WD881 was proved to be more toxic to all the algal test species than Fire-Brake™ 3150A. Among fire retardants/suppressants, Phos-Chek® Insul-8 was more toxic than Phos-Chek® MVP-F. Algae such as *S. capricornutum* and *C. vulgaris* were previously reported to be sensitive to fluorosurfactants such as PFOS (Boudreau et al. 2003). From the results it is clear that non-fluorosurfactant firefighting compounds are also capable of causing growth inhibition in algae. The toxicity was in the following order: Phos-Chek® WD881 > Fire-Brake™ 3150A > Phos-Chek® Insul-8 > Phos-Chek® MVP-F. Among algae, *D. tertiolecta* and *R. subcapitata* were very sensitive to Class A firefighting compounds tested in this study.

Table 1. Acute toxicity of bush firefighting compounds to alga.

Compounds	**EC_{50} (%)**		
	R. subcapitata	***C. vulgaris***	***D. tertiolecta***
Phos-Chek® WD 881	0.01 (0.009 - 0.011)	0.018 (0.016 - 0.019)	0.002 (0.0018 - 0.0021)
Fire Brake™ 3150A	0.015 (0.014 - 0.017)	0.113 (0.106 - 0.122)	0.0034 (0.0032 - 0.0037)
Phos-Chek® MVP-F	0.042 (0.039 - 0.045)	0.291 (0.268 - 0.316)	1.48 (1.37 - 1.60)
Phos-Chek® Insul 8	0.026 (0.024 - 0.028)	0.168 (0.154 - 0.183)	1.18 (1.09 - 1.28)

EC_{50}: Effective concentration of the firefighting product causing 50% inhibition in the growth of the alga; values in parenthesis represents 95% confidence limits; values in parenthesis represents 95% confidence limits.

CONCLUSIONS

Evidently both Phos-Chek® WD881 and Phos-Chek® Insul-8 were found to be comparatively more toxic to all the algal species tested. To the best of our knowledge this is the first report on the acute toxicity of Class A and bush firefighting compounds to algae representing fresh water, soil and marine water.

REFERENCES

Boudreau, T.M., Sibley, P.K., Mabury, S.A., Muir, D.G.C. and Solomon, K.R. (2003) Laboratory evaluation of the toxicity of perfluorooctane sulfonate (PFOS) on *Selenastrum capricornutum*, *Chlorella vulgaris*, *Lemna gibba*, *Daphnia magna*, and *Daphnia pulicaria*. Arch. Environ. Con. Toxicol. 44(3): 0307-0313.

Ji, J., Long, Z., and Lin, D. (2011) Toxicity of oxide nanoparticles to the green algae *Chlorella* sp. Chem. Eng. J. 170(2): 525-530.

Megharaj, M., Singleton, I., McClure, N.C. and Naidu, R. (2000) Influence of petroleum hydrocarbon contamination on microalgae and microbial activities in a long-term contaminated soil. Arch. Environ. Con. Tox. 38: 439-445.

Poulton, B.C. (1996) Effects of two fire suppressant foams on benthic invertebrates colonizing artificial substrates in portable limnocorrals. *Proc. N. D. Acad. Sci*. 50: 145-149.

Vyas, N.B., Spann, J.W. and Hill, E.F. (2009) Acute oral toxicities of wild land fire control chemicals to birds. *Ecotox. Environ Safe*. 72(3): 862-865.

REMBIND USED TO TREAT FIREFIGHTING FOAM CONTAMINANTS

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INTRODUCTION

An independent study was commissioned by a government airport authority in Australia to validate the effectiveness of RemBind to treat Aqueous Film Forming Foams (AFFF) contaminants in soil. AFFF contaminants include perfluorooctane sulfonate (PFOS) which was listed in 2009 as a chemical of major concern by the Stockholm Convention on persistent organic pollutants.

The trial was independently supervised and audited by the environmental consulting company SEMF. This included sealing sample containers, doorways and fume cupboards at the end of each trial day to maintain integrity of the process.

METHODS

PFOS contaminated soil was collected from two different commercial airport sites in Australia and sent to Ziltek's laboratory for processing (designated Soils 1 and 2).

Soils were air-dried, thoroughly mixed and screened in preparation for the treatment trials. RemBind or RemBind Plus was added to the soils at various rates and, after moisture adjustment, treatments were left to cure for 48 hours.

Treated samples (and untreated controls) were sent to an accredited commercial laboratory for leachability testing using ASLP (Australian Standard Leaching Procedure, based on US EPA Method 1311) for PFOS and PFOA (perfluorooctanoic acid). Selected samples were subjected to the more rigorous Multiple Extraction Procedure (MEP; US EPA Method 1320) to test for longevity of binding.

RESULTS AND DISCUSSION

A summary of the results are presented in Tables 1 to 3 below. Results show that PFOS leachability was reduced by more than 98.5% for soil from both sites. PFOA leachability reductions followed a similar trend. For both soils, RemBind Plus reduced PFOS leachability to below the stringent Minnesota Department of Health drinking water guidelines of 0.3ug/L.

MEP results show that Soil 1 treated with RemBind Plus passed the stringent MEP test which stimulates 1,000 years of acid rain in an improperly designed sanitary landfill.

Table 1. Leachability reduction of PFOS and PFOA for Soil 1

Site 1	ASLP Analysis			
	PFOS ug/L	%	PFOA ug/L	%
Untreated Soil	34.15	-	0.65	-
RemBind	0.50	98.5	0.04	93.8
Rembind Plus	0.29	99.2	<0.02	>96.9

Table 2. Leachability reduction of PFOS and PFOA for Soil 2

Site 2	ASLP Analysis			
	PFOS ug/L	%	PFOA ug/L	%
Untreated Soil	376	-	5.51	-
RemBind	1.76	99.5	0.27	95.1
Rembind Plus	0.10	99.9	<0.02	>99.6

Table 3. Multiple Extraction Procedure results for Soil 1 treated with RemBind Plus

					Site 1 – RemBind Plus Treatment					
Leach	**EP**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
PFOS ug/L	0.04	0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02

For treatments that included 5% Portland cement as a stabilising agent, the leachability of PFOS/PFOA was significantly higher. It is understood that these compounds will leach more readily from soils at a higher pH due to their chemical make-up. At low pH, soil particle surfaces are more positively charged resulting in adsorption of PFCs which have a net negative charge. At high pH, the soil particle surfaces are more negatively charged and electrostatic repulsion suppresses the sorption of PFCs (Johnson et al. 2007; Xiaodong and Chrover, 2012).

CONCLUSIONS

In conclusion, this was a totally independent study that showed that RemBind Plus treatments reduced PFOS leachability by >99.2% to below the Minnesota drinking water guidelines of 0.3ug/L and that this binding was stable long-term as determined by the most stringent soil leachability test available (US EPA Method 1320). The addition of Portland cement is detrimental to this process due to the high pH – these conditions are unlikely to be encountered in most environmental situations.

REFERENCES

Xiaodong, G., and Chorover, J. (2012), "*Adsorption of perfluorooctanoic acid and perfluorooctanesulfonic acid to iron oxide surfaces as studied by flow-through ATR-FTIR spectroscopy*". Environ Chem, Vol 9, pp. 148-157.

Johnson, R. L., Anschutz, A. J., Smolen, J. M., Simcik , M. F., Penn, R. L. (2007), "*The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces*". J. Chem. Eng, vol 52, pp. 1165.

The Minnesota Administrative Rules 2009 (March 2009).

CELL FIXATION TECHNIQUE FOR MICROSCOPIC VISUALISATION AND ELEMENTAL PROFILING OF CLAY-BACTERIAL HUTCH

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INTRODUCTION

Clay minerals (e.g., kaolinite, bentonite, palygorskite, etc.) possess high surface area, cationic exchange capacity and surface charge density, which are important for their applications in contaminant remediation. The remediation of organic contaminants (e.g., hydrocarbons and volatile organic compounds) is often pursued by microbial degradation. For a more effective and *in situ* biodegradation, the degrading microorganisms (e.g., bacteria and fungi) can be supported on clay minerals for a better proliferation and protection from potential toxic substances and predators (Sarkar et al., 2012). Clay minerals can provide both growth-enhancing supplement and protective shield, which can induce the formation of 'clay-bacterial hutch', and finally the clay-based biofilm (Lünsdorf et al., 2000). However, how these biotic and abiotic entities interact in such a microhabitat is not fully understood. Thus, for understanding their interaction in microscopic scale, imaging tools such as Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) are commonly used, especially to visualise the bacterial adhesion on clay surfaces. However, the procedures involved in sample preparation may destroy the 'clay-bacterial hutch', which creates significant artefacts in the assessment of clay-bacterial interaction. Fluorescence staining technique (e.g., membrane-impermeable dye propidium iodide, membrane-permeable dye SYTO 9) has also been applied to visualise such clay-bacterial mat by using fluorescence microscope (Alimova et al., 2007). However, the organic dyes may create additional artefacts and limitations, e.g., dye itself can bind with clay surfaces, which prevents proper distinguishability between clay particles and bacterial cells in a micro-aggregate, and the elemental profile/mapping of clay minerals provides an unresolved image. Staining or chemical fixation technique can still be useful, but it requires the appropriate selection of the staining agent which stains only the bacterial cells without binding to the clay minerals. More importantly, the stain should not contain any elemental component which is present in the bacterial cell substance (e.g., oxygen and nitrogen). Therefore, a metal(loid)-based cell-fixation compound, osmium tetroxide (OsO_4), which has bacterial cell-permeability and can bind with cellular lipid materials, was selected in order to study the interaction of a bacterium (*Burkholderia sartisoli*) with a bentonite clay.

MATERIALS AND METHODS

A pre-grown bacterium (*Burkholderia sartisoli*) was harvested at log growth phase and washed with saline water. Bacterial suspension (OD_{600}) (1 mL) was mixed with 0.1% (m/v) of bentonite suspension in sterile Milli-Q water to make a total 20 mL volume. A clay suspension without bacteria and a bacterial suspension without clay served as the controls. All the suspensions were incubated for 2 h followed by the fixation with 4% paraformaldehyde, 1.25% glutaraldehyde, 4% sucrose. A post-fixative treatment with 2% OsO_4 solution was then applied for 30 min. The samples were dehydrated with 70–100% ethanol, air-dried and coated with 40 nm pulsed carbon prior to imaging under SEM-EDAX (FEI Quanta 450 FEG Scanning Electron Microscope).

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RESULTS AND DISCUSSION

The OsO_4 fixation procedure did not allow the clay to bind Os on its surface (Fig. 1). However, the bacterial cells underwent strong binding with Os as detectable in the EDAX line profile (Fig. 2). These two properties of OsO_4 enabled to investigate the elemental distribution profile in the clay-bacterial aggregates more distinguishably. In the clay-bacterial complex, Si peak represents the presence of bentonite and Os signal comes from an aggregate where bacteria is present (Fig. 3). Interestingly, N, which is an integral component of cellular materials, plays another distinguishing role for bacteria (Fig 2 & 3). Osmium (Os), therefore, can be a unique fixative element to distinguish between clay particle and bacterial cell in a 'clay-bacteria hutch' at a microscopic scale, while the presence of N in bacteria further supports this evidence.

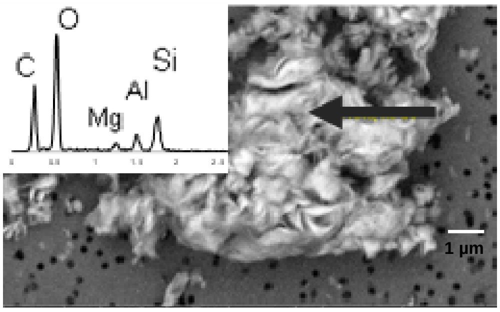

Fig. 1. No Os is absorbed on clay minerals

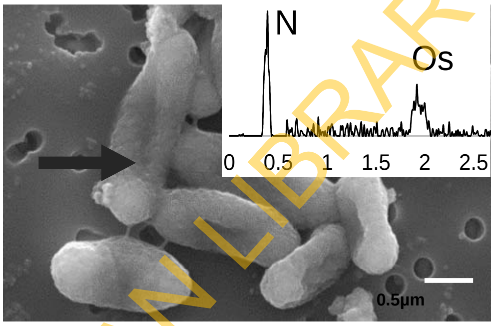

Fig. 2. Os and N are dominant signal from bacteria

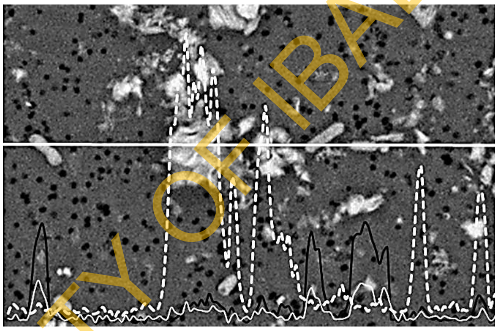

Fig. 3. A clay-bacterial complex shows distinct signal for each entity over the (white straight) line (dot white line=Si, black line=N, white line=Os)

CONCLUSION

An efficient method was developed in order to visualise the clay-bacterial interaction under SEM along with a strong evidence of elemental profile of the individual components. This technique has potential application in the investigation of complex clay-bacterial distribution in environmental samples.

REFERENCES

Alimova A. Roberts M. Katz A. Rudolph E. Steiner JC. Alfano RR. and Gottlieb P. (2006) Effects of smectite clay on biofilm formation by microorganisms. *Biofilm* 3:47–54.

Lünsdorf E. and Abraham T. (2000) Clay hutches': a novel interaction between bacteria and clay minerals *Environ. Microbiol.* 2: 161–168.

Sarkar B. Xi YF. Megharaj M. Krishnamurti GSR. Bowman M. Rose H. and Naidu, R. (2012) Bioreactive organoclay: a new technology for environmental remediation. *Crit. Rev. Environ. Sci. Technol*. 42:435–88.

SCREENING OF CATION DOPED HYDROXYAPATITE FOR STRONTIUM REMOVAL FROM AQUEOUS SOLUTIONS

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INTRODUCTION

Strontium contamination in ground and other water sources has been reported in many countries. Elevated level of strontium in ground water has been reported in various countries like USA, Jordan and Japan. In India, strontium contamination in water has been reported in areas like Cuddapah, Nellore, Prakasam and Srikakulam districts in Andra Pradesh and in Hoshiarpur and Nawanshahr districts of Punjab state (Bhalla *et al.*, 2011). It has led to rise in many diseases including neurological disorders Subsequently, EPA has recommended a permissible limit of 4.0 mg/L in drinking water.

Various treatment technologies have been studied to remove strontium from water. The common methods investigated are coagulation, flocculation, adsorption, electrocoagulation, oxidation/reduction reactions, nanofiltration, ion exchange etc. Among them, adsorption is considered to be less expensive and efficient method to control the mobility and bioavailability of strontium. However, there are few disadvantages of these adsorbents. The reusability and disposal of adsorbents have been a problem always. Hence many researchers are trying to improve the adsorption capacity, reusability and to disposal it in an eco-friendly manner. In this study, we developed an ecofriendly cation doped hydroxyapatite (HAp) with high surface area, biocompatibility and reusability having increased potential to adsorb strontium from aqueous solution.

METHODS

Synthesis of doped HAp

Four different cations viz, sodium, magnesium, aluminium and silica were used for doping HAp. 0.2 M of the respective salts were incorporated into 0.6 M solution of calcium nitrate individually. The mixtures containing both the solutions were stirred for 1 h. The solution was then added drop wise into 0.4 M solution of diammonium hydrogen phosphate. The reaction was performed at a pH greater than 9 with constant stirring for 2 h. The precipitate obtained was filtered and washed with copious amount of distilled water, dried overnight at 50 °C and calcined in air at 800 °C for 2 h. The doped cations were engineered to substitute for the calcium site in HAp lattice to obtain a composition in terms of (Ca + Na)/P, (Ca + Mg)/P, (Ca + Al)/P and (Ca + Si)/P with a molar ratio of 1.67.

Characterization of cation doped HAP

The synthesised HAp was characterised using suitable techniques like FTIR, XRD, FE-SEM, and XPS to understand its chemical, physical and structural properties. Biodegradability of the materials were studied in 0.05 M tris-HCl buffer solution at pH 7.4 for 15 days. The biocompatibility was assessed using MG-63 Human osteoblast cell lines in DMEM medium.

Screening for strontium adsorption capacity

The doped HAp materials were used to screen its strontium adsorption property. The adsorption studies were performed by keeping 10 ppm as the initial strontium concentration, 0.1 mg/mL as the adsorbent dosage and 3 h as the standard reaction time for all the samples. The samples were filtered using 0.2 µ filter and the filtrate was used to estimate the residual strontium using ICP-OES. Adsorption efficiency was calculated as percentage removal.

RESULTS AND DISCUSSION

The characterization studies like XRD, FTIR and XPS confirmed the elemental composition, crystallinity and phase purity of the HAp. The crystallinity of the HAp was found to increase on calcination at 800 °C, whereas before calcination the particles existed in amorphous state. Doping with cations was also found to improve the crystallinity of the HAp. Biodegradability of the uncalcined material was 19.05±2.33, 12.73±1.8, 20.19±2.7, 27.30±2.6 and 24.68±3.3 % in the native HAP, Na, Mg, Al and Si doped HAp respectively on incubation in tris-HCl for 15 days. On calcination, the biodegradability reduced considerably. The percentage removal of strontium using doped and uncalcined HAp was higher when compared to the control, doped and calcined HAp (Table 1). Uncalcined Al-HAp and Mg-Hap showed maximum strontium removal when compared to other HAp. The adsorption of strontium by these HAp particles might be due to surface adsorption or substitution at the crystal lattices. Strontium forms surface complexes with calcium and other reactive sites. During XPS studies, new peak formed at 270.81 and 23.76 eV were assigned to Sr 3p and Sr 4p (Xia *et al.,* 2010) (Fig. 1). Al doped HAp was found to be toxic than all other HAp when tested with MG63 osteoblast cells.

Table 1: Strontium adsorption by various HAp adsorbents

Material	% removal
Control HAp (uncalcined)	26.23 ± 0.79
Control HAp (calcined)	25.92 ± 0.21
Na-HAp (uncalcined)	51.68 ± 0.43
Mg-HAp (uncalcined)	70.98 ± 2.74
Al-HAp (uncalcined)	83.90 ± 3.03
Si-HAp (uncalcined)	35.80 ± 0.38
Na-HAp (calcined)	20.17 ± 0.07
Mg-HAp (calcined)	35.89 ± 1.11
Al-HAp (calcined)	63.24 ± 2.42
Si-HAp (calcined)	9.19 ± 3.08

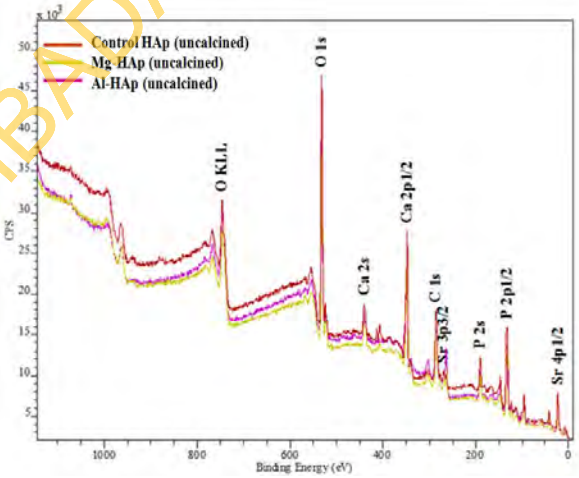

Fig. 1. XPS spectra of materials after Sr^{2+} adsorption

CONCLUSIONS

This study clearly indicates that uncalcined doped HAp nanoparticles with amorphous nature are well suited for strontium adsorption than calcined doped crystalline HAp nanoparticles. The morphology of the particles changes with doping and calcination. Among the doping, Mg and Al doping was found to suitable for strontium adsorption. However considering the toxicity of Al doped HAP, Mg doped HAp is a preferable adsorbent for strontium removal from aqueous solution.

REFERENCES

Bhalla, Uranium and strontium in ground water-logging in malwa region. Scientific opinion & fact sheet, 2011 (www. *physics.puchd.ac.in/dmehta/**uranium-facts**-201207.pdf)*

Xia W, C. Lindah, C. Persson, P.Thomsen, J. Lausmaa, H. Engqvist (2010). Changes of Surface Composition and Morphology after Incorporation of Ions into Biomimetic Apatite Coatings. J. Biomat. Nanobiotechnol. 1: 7-16.

NANOMATERIALS FOR PHOSPHORUS RECOVERY: SYNTHESIS, CHARACTERISATION AND MECHANISMS.

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INTRODUCTION

Phosphorus (P) is an important macro-nutrient essential for all living organisms. In general, P use efficiency by biota is low and only 15-20% of applied P is used by the crops and animals, the remaining amounts are released into various waste streams (Karunanithi et al., 2015). Globally, livestock production, domestic and industrial water consumption produce large quantity of manure and effluents (waste streams) which are rich in P and other nutrients (Rittmann et al., 2011). The P present in these waste streams pose a major threat to environment by way of nutrient enrichment resulting in various ecological problems such as eutrophication of waterways (Sharpley et al., 2001). Nanomaterials are potentially effective in the recovery of P from these waste streams which can be reused as a nutrient source for crops and animals.

METHODS

Nanomaterials such as clay, ZVI, FeO, Iron oxide, and hydroxy apatite are synthesised by sol-gel method and characterised by SEM, EDX, XRD, FTIR etc. These nanomaterials are used for P recovery experiments using synthetic P solution and waste streams. Adsorption and kinetics experiments are conducted to know the feasibility of P recovery.

RESULTS AND DISCUSSION

Adsorption experiment was conducted at different initial P concentration and after 24 h of equilibration, P content in original solution was measured by molubdate blue colour method and adsorption P onto nanomaterials was calculated. The adsorption data were fitted into Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherms were well fitted to adsorption isotherm data (R^2 value 0.97 and 0.99, respectively). However, Freundlich matched the experimental data better than Langmuir indicating that the adsorption of the P was controlled by heterogeneous process and the Q_{max} value for allophone nano clay was 34.48 mg/g. This result is comparable with other results in the literature.

Different rate-based and diffusion-based kinetic models were derived to understand the P adsorption mechanism on nanomaterials. The pseudo-second order matched better than the Pseudo first order (R^2 value 0.97 and 0.69, respectively) indicating inadequacy of pseudo first order to explain all the adsorption process. The Elovich and intra-particle diffusion models were also well fitted to the kinetic data which suggested that the chemisorption and pore diffusion were the dominating mechanisms of P adsorption onto nanomaterials. Similar results were reported by other authors.

Table 1. Selected properties of nanomaterials.

Nano materials	Particle size (nm)	Total pore volume ($m^2 g^{-1}$)	Surface Area ($m^2 g^{-1}$)	Zeta potential (mV)
Allophane	90-500	0.059	21.15	-20.76
ZVI	54-290	-	12.00	19.54
FeO	12-154	-	-	-26.35
Iron oxide	34-163	0.040	16.96	-18.09
HAP	20-54	0.043	21.83	-12.35

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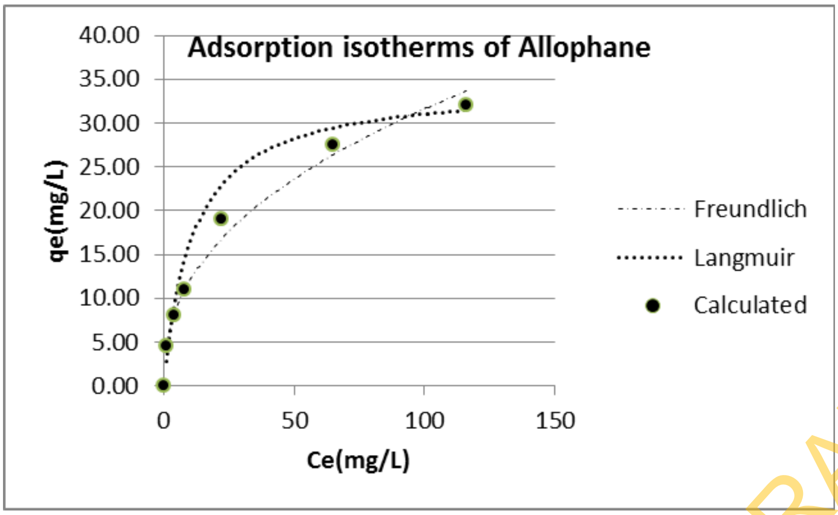

Fig. 1. Adsorption isotherms for Allophane nanoclay

CONCLUSIONS

Nanomaterials can be used as low cost adsorbent for the recovery of P from waste streams.

REFERENCES

Karunanithi, R., Szogi, A., Nanthi Bolan, Ravi Naidu., Loga Loganathan, John Hunt, Matias Vanotti, Christopher Saint, Yong Sik Ok and Sathiya Krishnamoorthy (2015). Phosphorus recovery and reuse from waste stream. *Advn. Agron.*131, pp. 1-78.

Rittmann, B. E., Mayer, B., Westerhoff, P., and Edwards, M. (2011). Capturing the lost phosphorus. *Chemosphere* 84:846-853.

Sharpley, A. N., McDowell, R. W., and Kleinman, P. J. (2001). Phosphorus loss from land to water: integrating agricultural and environmental management. *Plant Soil* 237:287-307.

NANO-ENCAPSULATED PESTICIDES: DREAM OR NIGHTMARE, AN ENVIRONMENTAL ASPECT

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INTRODUCTION

Globally, huge amounts (~2 million metric tons per year) of pesticides are applied to prevent the crop loss caused by pests. More than 90% of the applied pesticides are lost into the environment without any contribution in pest control. Thus, hundreds of chemicals are introducing into the environment, results in unfavourable effects either to living beings or to the environment including soil and water pollution. Therefore, the safe application of pesticides is a burning issue of current research. Nanotechnology is considered as one of the latest technology of current era and researchers from all over the world are trying to utilize this technology to overcome the drawbacks of conventional pesticides. So far, the most potential application of this technology have been explored as nano-carrier or nano-encapsulation materials for the pesticides to increase their efficacy and improve their properties (e.g, slow release, protection against premature degradation). Whereas the impact of nano-encapsulated pesticides, especially nano-encapsulation materials' still unclear and the introduction of nano-encapsulated pesticides in agricultural practices may be both new risk and new benefits to human and environment (Kah et al. 2013). Still there is no standard regulatory protocol to determine the fate of nano-encapsulated pesticides. Therefore, it is important to assess the probable environmental fate of nano-encapsulated pesticides or the nano-carrier materials and find out the suitability of the parameters required to develop regulatory framework.

NANO-ENCAPSULATED PESTICIDES

Nano-encapsulated pesticides considered as the formation of pesticide loaded or entrapped particles having a diameter within the nano-range. The encapsulated material is commonly referred to as the internal phase, the core material, the filler or the fill, for instance pesticides. The encapsulation material is known as the external phase, the shell, coating or membrane e.g., nano-capsules. So far, various nano-encapsulation materials have shown their efficacy to encapsulate the pesticides (Fig.1). In this content, the suitability of these encapsulated materials will be analysed based on their probable environmental fate.

Environmental Fate of Nano-encapsulated Pesticides

The investigation of environmental fate of nano-encapsulated pesticides has rarely studied and more complex in soil than water. Each of the nano-encapsulation material's properties are different in different environmental condition whereas their fate into the environment depend on the physical properties (e.g, ionic strength, particle size). Till to date, the environmental fate of nano-encapsulated pesticides have been investigated as their toxicity level to soil and aquatic organisms.

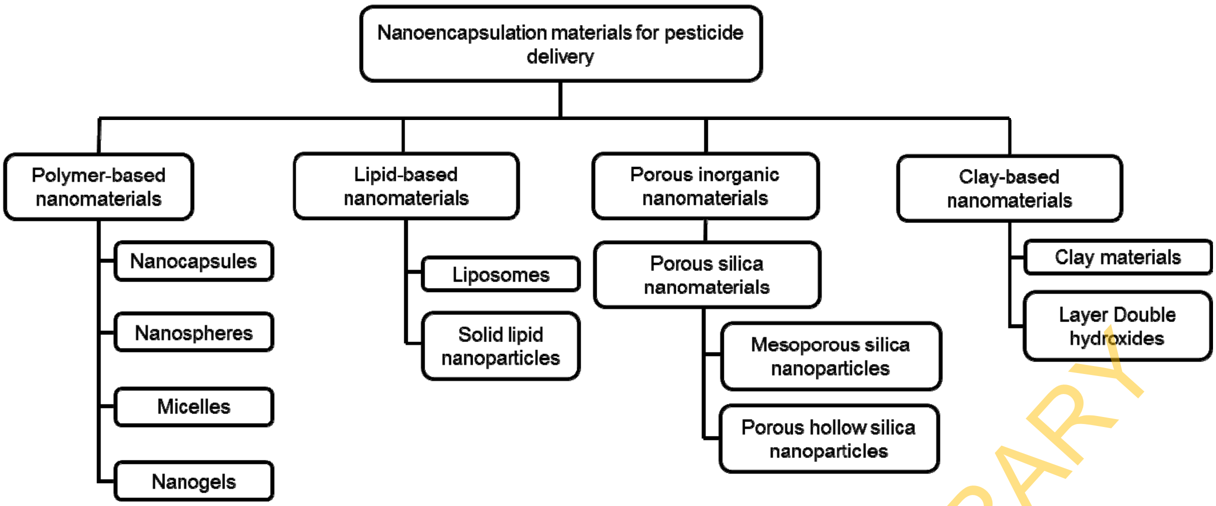

Fig. 1. Promising nano-encapsulation materials used for pesticide delivery

CONCLUSIONS

Nano-encapsulated pesticides are expected to be eco-friendly compare to the commercial pesticides. More investigation is required to investigate the fate of nano-encapsulation materials in the environment for which more analytical techniques are required for detection, characterization and quantify the nano-encapsulation materials.

REFERENCES

Kah, M., Tiede, K., Beulke, S. and Hofmann, T. (2013). Nanopesticides: state of knowledge, environmental fate and exposure modelling. *Crit. Rev. Env. Sci. Technol*. 43:1823–1867

STAINLESS STEEL NANOTUBE AS A PHOTOCATALYST FOR WASTEWATER TREATMENT

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INTRODUCTION

Photocatalyst has been attracting interests because of their wide application to environmental remediation. Metal oxide semiconductors, such as TiO_2, WO_3, Fe_2O_3, and so on, were used for photocatalyst due to distinctive properties and durability(Mano et al., 2015). Especially iron based materials is applicable to real fields because of their cost effectiveness. To improve photocatalytic acitivity, iron based materials can be easily modified to nanoparticles, nanoalloys, nanotubes, etc (Ahmed et al., 2014). Moreover, efficiency of iron based photocatalyst can be further enhanced together with hydrogen peroxide or ozone used as sensitizer to activate generation of OH· radicals. In this research, we fabricated stainless steel nanotube (SSNT) by anodization and tested its use with UV and ozone.

METHODS

Fabrication

Stainless steel (99%, Korea) was synthesized to SSNT by anodization at various conditions. The electrolyte was perchloric acid based on ethylene glycol. Different perchloric acid concentration of 1%, 3%, and 5% were used in anodization to select optimal fabrication concentration. Other anodization conditions, such as temperature (5°C, 20°C), time (10 - 20min), and so on, were also tested..

Characterization

Fabricated SSNT crystal structure was verified with X-ray Diffraction (XRD). The nanotube size and contained atoms of SSNT was measured with scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). Surface morphology was investigated with Atomic Force Microscopy (AFM).

Photocatalytic activity

Total organic concentration (TOC) of the tested wastewater was 25mg/L and chemical oxygen demand (COD) was approximately 100mg/L. Two hundred and fifty milliliter of the wastewater were used for degradation test with SSNT, UV (30W), and ozone. Ozone was produced by an ozone generator (Azcozon) continuously bubbled into the reactor. Dissolved ozone concentration was 2.86mg/L. Degradation experiment was performed for 60min and sampling was conducted every 10min.

RESULTS AND DISCUSSION

Figure 1 illustrates the obtained SEM images at various anodization conditions. In result, showed most uniformly distributed holes appeared on the surface at 5% perchloric acid, anodization (5°C) for 10min at 40V constant voltage. Figure 2 showed the result of TOC degradation experiment. The SSNT improved the photocatalytic activity with ozone and UV in both TOC and COD decrease. However, there was no degradation of TOC with SSNT only. Adsorption of organic compounds onto SSNT was negligible.

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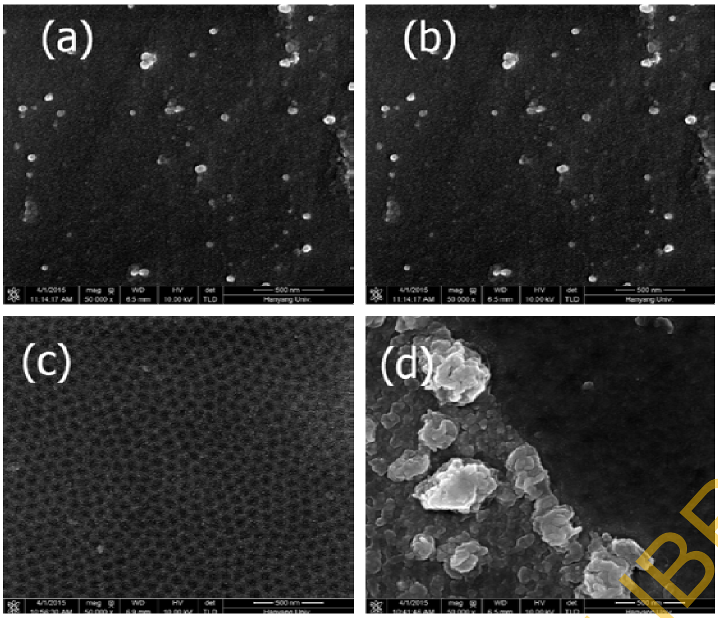

Figure 1. SEM images of the stainless steel after anodization: (a) 1%, 10minutes, (b) 3%, 10minutes, (c) 5%, 10minutes, and (d) 5%, 20minutes calcination (at 400°C, 8hours).

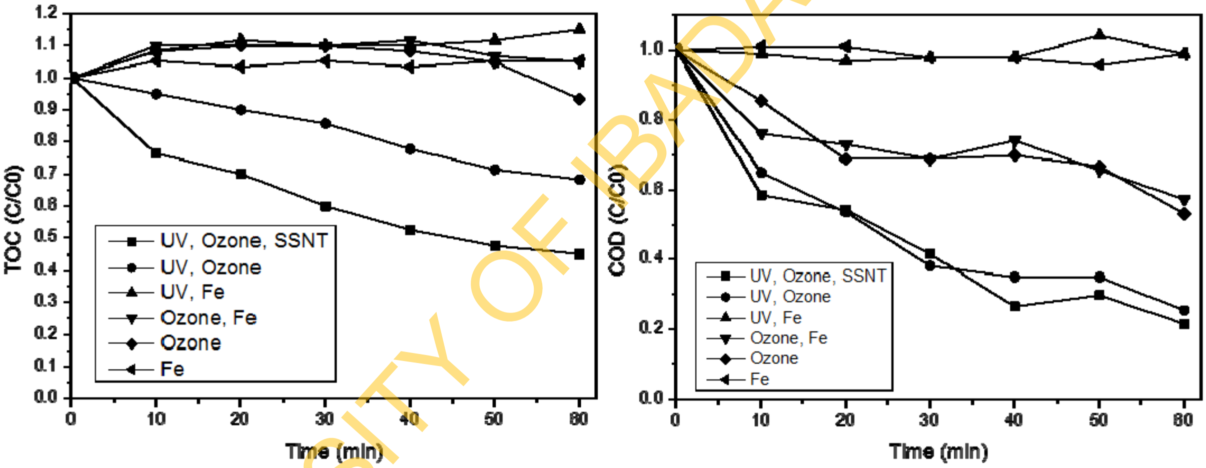

Figure 2. Concentration change of TOC and COD with UV, Ozone, and SSNT.

CONCLUSIONS

SSNT fabricated at 40V, 10min, 5% (perchloric acid) showed best uniformly porous nanotube shape in SEM image. With UV, ozone, and SSNT, degradation of both TOC (55%) and COD (78%) were observed. This result indicates that SSNT can improve the photocatalytic activity with ozone and UV.

REFERENCES

AHMED, F., ARSHI, N., ANWAR, M. S., DANISH, R. & KOO, B. H. 2014. Quantum-confinement induced enhancement in photocatalytic properties of iron oxide nanoparticles prepared by Ionic liquid. *Ceramics International,* 40**,** 15743-15751.

MANO, T., NISHIMOTO, S., KAMESHIMA, Y. & MIYAKE, M. 2015. Water treatment efficacy of various metal oxide semiconductors for photocatalytic ozonation under UV and visible light irradiation. *Chemical Engineering Journal,* 264**,** 221-229.

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SILVER SILICATE MODIFIED GRAPHITIC CARBON NITRIDE AS NOVEL PHOTOCATALYSTS

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INTRODUCTION

Advanced oxidation processes (AOPs) have been widely investigated and employed as a viable strategy to degrade organic compounds in wastewater into simple compounds, carbon dioxide and water. Currently, photocatalytic abatement of organic pollutants has drawn extensive interest from both academic and industrial societies. Graphitic carbon nitride (g-C_3N_4) has been considered as one of the most eminent candidates due to its low toxicity, high stability and appealing electronic structure. Nevertheless, the photocatalytic activity is limited by its low surface area and quantum efficiency. Many potential modifications of g-C_3N_4 have been carried out in activity improving. (Sun, et al., 2014; Ai, et al., 2014)

Silicates have been widely employed as industrial catalysts. A silicate-based photocatalyst has been reported recently owing to desirable photocatalytic activity. $Ag_6Si_2O_7$ has an internal polar electric field by controlling the array of the polar SiO_4 tetrahedra, which coordinate Ag^+ ions leading to AgO_x. $Ag_6Si_2O_7$ exhibits a very high potential in photocatalytic application due to its response in whole visible-light region ($\lambda < 740$ nm). (Lou, et al., 2014)

In this study, g-C_3N_4/$Ag_6Si_2O_7$ composites would be synthesized. These composites were tested in photocatalytic degradation of methylene blue under UV-vis light. Furthermore, their physicochemical properties, such as crystalline structure and morphology were observed.

METHODS

Materials and Synthesis

Synthesis of $Ag_6Si_2O_7$: In detail, 0.852g Na_2SiO_3•$9H_2O$ was dissolved in 210 ml deionized water under continual stirring. Then the mixture was added gently into 90 ml 0.1M $AgNO_3$ solution to generate reddish brown precipitates. After 30 min stirring, the precipitates were harvested from the solution by vacuum filtration and washed with deionized water for 3 times before drying at 55 ℃ overnight.

Synthesis of g-C_3N_4/$Ag_6Si_2O_7$: 0.284g Na_2SiO_3•$9H_2O$ was dissolved with the 70ml deionized water under continual stirring, then 3.672 g of prepared g-C_3N_4 were added into the solution under ultrasonic treatment for 60 min. The mixture was added gently into 30ml 0.1M $AgNO_3$ solution to generate orange precipitates. After 30 min stirring, the precipitates were harvested from the solution by vacuum filtration and washed with deionized water for 3 times before drying at 55 ℃ overnight. Several g-C_3N_4/$Ag_6Si_2O_7$ at different ratios were synthesised in the same way, and final precipitates were labelled as g-C_3N_4/$Ag_6Si_2O_7$-20%, g-C_3N_4/$Ag_6Si_2O_7$-30%, g-C_3N_4/$Ag_6Si_2O_7$-40%, and g-C_3N_4/$Ag_6Si_2O_7$-50%.

Characterization of Materials

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 diffractometer (Bruker-AXS, Karlsruhe, Germany). The structure and morphology of the materials were performed on a scanning electron microscopy (SEM, Zeiss Neon 40EsB FIBSEM). UV-vis diffuse reflectance spectra (DRS) of prepared catalysts were recorded on a JASCO V670 UV-vis spectrophotometer with an Ø 60 mm integrating sphere, in which $BaSO_4$ was used as a reference standard.

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Photodegradation of Methylene Blue

The aqueous photocatalytic oxidation of methylene blue was carried out in a 1000 mL double-jacket cylindrical Pyrex vessel reactor. A water bath connected with a pump was used to control the reaction temperature at 30℃ by recycling the cooling water. The light source was set about 30 cm from the liquid surface of the suspension. The irradiation source was supplied by a MSR 575/2 metal halide lamp (575 W, Philips). In detail, 0.1g of photocatalyst was added into 200 mL of 10 ppm methylene blue solution and stirred 30 min to achieve the adsorption-desorption equilibrium. The light was immediately switched on, and then reaction was started by exposing the UV-vis irradiation. During the process, 3 mL of solution was collected and centrifuged at each time interval, and then analysed by a JASCO UV-vis spectrophotometer at 664 nm.

RESULTS AND DISCUSSION

XRD patterns g-C_3N_4, $Ag_6Si_2O_7$, and g-C_3N_4/$Ag_6Si_2O_7$ suggested that $Ag_6Si_2O_7$ dopant has some effects on the XRD pattern of g-C_3N_4. Strong g-C_3N_4 and $Ag_6Si_2O_7$ peaks can be found in g-C_3N_4/$Ag_6Si_2O_7$ composites at 27.4° and 34.8°, respectively. For UV-vis spectra of g-C_3N_4 and g-C_3N_4/$Ag_6Si_2O_7$-50%, a strong broad band centred at around 400 nm. The g-C_3N_4 exhibits absorption onsets at 460 nm, is corresponding to the band gap at 2.63 eV, and the band gap of g-C_3N_4/$Ag_6Si_2O_7$-50% composites is 2.58 eV. Fig. 1(A) shows that various ratios of g-C_3N_4/$Ag_6Si_2O_7$ composites can make a complete decomposition of methylene blue in 180 min. Among them, the g-C_3N_4/$Ag_6Si_2O_7$ -50% could achieve 100% degradation under 120 min irradiation. It also can be seen from Fig. 1(B) that the pure $Ag_6Si_2O_7$ has the greatest photocatalytic activity for methylene blue removal, which would degrade 100% methylene blue within 30 min. For pure g-C_3N_4, only 20% of methylene blue was degraded at 30 min, and achieved 80% degradation at 180 min under UV-vis light irradiation.

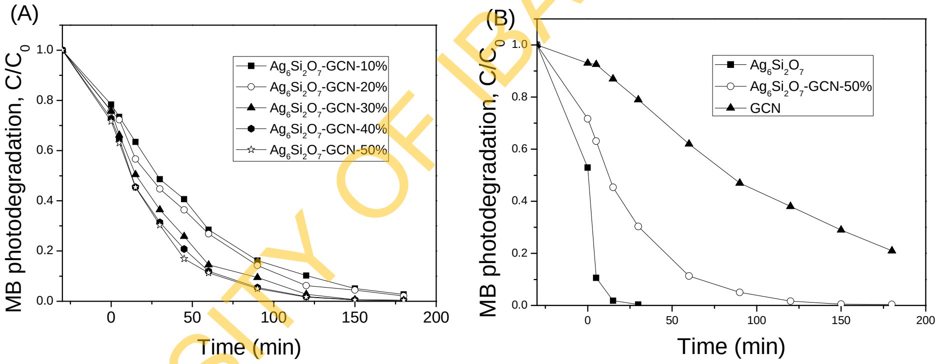

Fig. 1. Photodegradation of methylene blue on (A) different g-C_3N_4/$Ag_6Si_2O_7$ composites and (B) g-C_3N_4 and $Ag_6Si_2O_7$ under UV-vis light irradiations.

CONCLUSIONS

g-C_3N_4/$Ag_6Si_2O_7$ composites were successfully synthesized using a facile hydrolysis and ion-exchange method. The photocatalytic properties were examined. The g-C_3N_4/$Ag_6Si_2O_7$ composites showed a high photocatalytic activity in decomposition of methylene blue under UV-vis light irradiations with relatively low adsorption of methylene blue.

REFERENCES

Sun, H., Zhou, G., Wang, Y., Suvorova, A., Wang, S. (2014) A New Metal-Free Carbon Hybrid for Enhanced photocatalysis. ACS Appl. Mater. Interfaces 6(19): 16745-16754.

Ai, B., Duan, X., Sun, H., Qiu, X., Wang, S. (2014) Metal-Free Graphene-Carbon Nitrides for Photodegradation of Organic Pollutants in Water. Catal. Today, in press.

Lou, Z.Z., Huang, B.B., Wang, Z.Y., Ma, X.C., Zhang, R., Zhang, X.Y., Qin, X.Y., Dai, Y., Whangbo, M.H. (2014) $Ag_6Si_2O_7$: a Silicate Photocatalyst for the Visible Region. Chem. Mater., 26(13): 3873-3875.

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NANO-ZERO VALENT IRON-DECORATED ELECTROSPUN MEMBRANES USING A COAXIAL ELECTROPINNING TECHNIQUE: PREPARATION AND GROUNDWATER REMEDIATION

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INTRODUCTION

The management of contaminated soil and groundwater is currently one of the major environmental issues (Cundy et al., 2008). Conventional remediation methods have been proven to be ineffective and less sustainable in various situations, thus, focus has been turned to the development of novel in-situ remediation technologies (Crane and Scott, 2012, Chekli et al., 2013). This study investigates a novel remediation technique for in situ groundwater clean-up of emerging contaminants through the use of nanotechnology. Manufactured nanoparticles (MNPs) are increasingly used for this application as they demonstrate great performance for the removal of a wide range of common soil and groundwater contaminants. However, one of the main issues related to this remediation technology is the high mobility of the MNPs in the subsurface and their potential to carry contaminants away from the contaminated zone. To overcome this issue, this study combined the fundamental science and engineering for the in situ treatment of groundwater by immobilizing nanoparticles onto nanofibrous mats through a coaxial electrospinning technique. Electrospinning is a versatile process in producing ultrafine fibers through the application of high voltage electric fields (Tijing et al., 2012). The remediation will be achieved by simple contact between the MNPs immobilised onto the surface of the nanofibrous mats and the contaminants are eventually decomposed or mineralised to harmless by-products.

MATERIALS AND METHODS

A coaxial electrospinning set-up composed of a coaxial metallic nozzle, high voltage power supply, syringe pump, plastic syringe, and drum collector, all enclosed in a sealed container was used in this study. The nano/micro fibers were electrospun at a voltage of 15-20 kV through a distance of 15 to 20 cm. Solution flow rates were maintained at 1 ml/h. Two different composite coaxial fiber membranes were fabricated: one (CM1) is where the sheath layer is composed of either a mixed poly(acrylic) acid (PAA) and polyvinyl alcohol (PVA) solution, and the core layer was made of nylon-6, and the other one (CM2) is a sheath layer of nano-zerovalent iron (nZVI) nanoparticles (NPs)/nylon-6 solution, and the core layer is nylon-6 solution. CM2 is a one-step process through incorporation of stabilized nZVI particles, while CM1 is a two-step process wherein the nZVI is selectively in-situ reduced on the surface of the fiber membrane. After electrospinning, the membranes were dried in an oven, or for the case PAA/PVA fibers, crosslinking was first carried out and immersion process for the reduction to nZVI.

The composite mats were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transfer infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), tensile and thermal stability testing, and degradation studies of different groundwater pollutants.

RESULTS AND DISCUSSION

The SEM results indicated fiber diameters ranging from 300 to 1100 nm with core-shell structures. CM1 showed widely distributed nZVI particles on the surface of the coaxial fibers, and no nZVIs were observed in the core of the fibers. This indicates the selective incorporation of the nZVIs only on the surface of the fibers, which facilitates the proper contact of the pollutants to be degraded to the immobilized particles on the surface. On the other hand, CM2 showed rougher surfaces, due to the formation of some agglomerates of the incorporation of the nZVIs through a simple blending technique. The results also indicate good dispersion of the nZVIs on the surface of the fibers. Some nZVIs were found to protrude on the surface, but still the lower part of the nZVIs are properly adhered on the fiber, making good immobilization and less chance of sloughing off. The TEM images also confirmed the observations of the SEM images and the presence of nZVIs on the surface.

Other characterization such as XPS, FTIR and XRD showed the existence of iron peaks in the spectra, which indicate the successful incorporation of the nZVIs on the fiber. Some slight shifting of the spectra was also observed, which tells that there was some interaction between the nZVIs and the host polymer that makes their immobilization adherent enough. The mechanical and thermal properties showed increased tensile strength and thermal stability when nZVIs were added in the composite membrane.

The degradation of some groundwater pollutants such as arsenic, copper, and trichloroethylene (TCE) using the composite membranes was investigated. The results showed that both CM1 and CM2 has comparable degradation performance for all pollutants, but are at a much higher efficiency compared to nZVI alone or polymer fibers alone. Several regeneration experiments were carried out and still high performance efficiency was achieved for the nZVI-decorated coaxial membranes, which is primarily attributed to the proper immobilization and dispersion of the nZVIs on the surface, and not at the core of the fibers. The use of nanofibers as host matrix provides very high surface area to volume ratio and high porosity for the nZVIs, thus enabling them to have good degradation performance. This technique of using coaxial electrospinning with nanoparticle decoration could find versatile application in groundwater remediation.

CONCLUSION

The present study investigated the feasibility of groundwater remediation through the use of selective immobilization of nZVIs on the surface of the fiber through coaxial electrospinning. The results in this study showed good dispersion and adherence of the nZVIs on the host matrix with very high surface, thereby making more contact area for degradation of pollutants such as arsenic, copper and TCE. The present simple technique could find potential application not only in groundwater remediation, but also in other applications that require good contact of the reactive nanoparticles, which are properly immobilized. Further studies are still needed to optimize the design and performance of the composite mats.

ACKNOWLEDGEMENT

This research was funded by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE).

REFERENCES

Chekli, L., Phuntsho, S., Roy, M., Lombi, E., Donner, E. & Shon, H. K. (2013). Assessing the aggregation behaviour of iron oxide nanoparticles under relevant environmental conditions using a multi-method approach. *Water Research* 47:4585-4599.

Crane, R. A. & Scott, T. B. (2012). Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *Journal of Hazardous Materials* 211-212:112-125.

Cundy, A. B., Hopkinson, L. & Whitby, R. L. D. (2008). Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Science of the Total Environment* 400:42-51.

Tijing, L. D., Ruelo, M. T. G., Amarjargal, A., Pant, H. R., Park, C. H., Kim, D. W. & Kim, C. S. (2012). Antibacterial and superhydrophilic electrospun polyurethane nanocomposite fibers containing tourmaline nanoparticles. *Chemical Engineering Journal* 197:41-48.

PREPARATION AND SURFACE MODIFICATION OF BIOCHAR FOR ENVIRONMENTAL REMEDIATION

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INTRODUCTION

Biochar (BC) is a carbon rich product which is produced as a by-product of thermal decomposition of various organic biomasses at low temperature (< 700 ˚C) in the absence of oxygen (Joseph et al. 2010). There have been increasing interests on using BC as a soil amendment because of its ability to provide agronomic benefits to plants by supplying nutrients to the roots and microorganisms directly from the source within itself, or indirectly by its ability to sorb and retain nutrients (Mandal et al. In press). On the other hand, application of BC can reduce the bioavailability of heavy metals such as chromium (Cr), lead (Pb), arsenic (As) and copper (Cu) in soils. The effectiveness of BC in nutrient and contaminant interactions largely depends on its specific characteristics such as, surface area, pore volume, pore space, functional groups, pH, cation exchange capacity (CEC) and electrical conductivity (EC). These characteristics of BC can be modified by using alternative materials such as chitosan, nano zerovalent iron (nZVI), hydrogen peroxide and some nano crystals (Zhou et al. 2014). The surface modified BC can serve as an environmental remediation agent by reducing heavy metal mobility and greenhouse gas (GHG) emissions. Heavy metals like Cr pose deleterious impact on the soil environment, crop yield and quality. There are two forms of Cr, less toxic trivalent chromium [Cr(III)] and highly toxic hexavalent chromium [Cr(VI)] (Choppala et al. 2012). This study provides an overview of synthesis and surface modification of manure based BC, and its subsequent value on Cr(VI) remediation in soils through reduction reaction.

METHODS

In this study two soils with varying pH values (Soil 1; pH 7.5 and Soil 2; pH 5.5) and three different manure samples including poultry manure (PM), cow manure (CM) and sheep manure (SM) were used. Biochar was produced through thermal decomposition (450 ˚C for 53 mins) of these manure samples. Chitosan and nZVI were used to modify BC. For this modification, chitosan was first dissolved in 2% acetic acid solution. Then nZVI particles were dispersed in chitosan solution followed by the addition of BC samples. The above suspension was drop wise added into 450 ml of 1.2% NaOH solution to achieve solidification. After decantation the solid portion was dried using a freeze dyer at -40 ˚C. Soil samples were spiked with 100 mg Cr(VI) kg^{-1} using $K_2Cr_2O_7$ solution at field capacity moisture level. The amendments were mixed with the soils at 5% level (w/w) and incubated for 33 days. Subsamples of amended soils were extracted with 1M KH_2PO_4 (1:10) to measure bioavailable Cr(VI) by spectrophotometric method at 540 nm.

RESULTS AND DISCUSSION

The surface area, pore volume, C% and S% of BC were greater than the initial manure sample. However, the modified BC showed a lesser surface area and pore volume than the BC sample due to blocking of pores by the chitosan molecules. Furthermore, application of BC and modified BC showed an increased Cr(VI) reduction as compared to manure application (Table 1).

Table 1: Surface characteristics of PM, manure based biochar and modified biochar, and their effect on Cr(VI) reduction in soil 1

Material	Properties							Maximum Cr(VI) reduction (mg kg^{-1})
	pH	EC (mS)	C%	N%	S%	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	
PM	8.36	3.56	20.16	2.22	0.47	3.97	0.002	46.2
PM-BC	10.28	0.28	27.27	2.10	0.55	4.92	0.012	78.9
PM-BC-M	10.47	0.83	11.37	1.29	0.19	2.64	0.004	88.9

The results indicated that modified BC application is more effective than BC application in achieving Cr(VI) reduction in soils. The effect of modified BC on enhanching Cr(VI) reduction is attributed to the presence of multiple surface functional groups (carbonyl, carboxylic, hydroxylic and phenol). Also, BC and modified BC have polycyclic hydrocarbon sheets which are highly porous. These sheets can act as an electron donor for the conversion of Cr(VI) to to Cr(III).

CONCLUSIONS

This study demostrated that modification of BC with chitosan and nZVI could improve the surface characteristics of the material which are favourable for the remediation of environmental pollutants like Cr(VI). Future study should explore the effect of different modification techniques for improving the material' remediation efficiency.

REFERENCES

Choppala, G. K., Bolan, N. S., Megharaj, M., Chen, Z. and Naidu, R. (2012) 'The Influence of Biochar and Black Carbon on Reduction and Bioavailability of Chromate in Soils', *J. Environ. Qual.,* 41(4), 1175-1184.

Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., Van Zwieten, L., Kimber, S., Cowie, A., Singh, B. P., Lehmann, J., Foidl, N., Smernik, R. J. and Amonette, J. E. (2010) 'An investigation into the reactions of biochar in soil', *Australian Journal of Soil Research,* 48(6-7), 501-515.

Mandal, S., Thangarajan, R., Bolan, N., Sarkar, B., Khan, N., Ok, Y. S. a. and Naidu, R. (In press) 'Biochar-induced concomitant decrease in ammonia volatilization and increase in nitrogen use efficiency by wheat', *Chemosphere*.

Zhou, Y., Gao, B., Zimmerman, A. R., Chen, H., Zhang, M. and Cao, X. (2014) 'Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions', *Bioresource Technology,* 152, 538-542.

THE IMPACT OF COMBUSTION ON SORPTION CAPACITY OF BIOCHAR FOR CADMIUM

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INTRODUCTION

In recent years, pyrogenic carbon (PyC) has been recognised as an active geosorbent for both organic and inorganic pollutants. Against this background, extensive research has been conducted on biochar, one form of synthetic PyC that is purposely engineered for both carbon sequestration and *in situ* stabilization of soil contaminants. Biochar is partially carbonized product generally manufactured under oxygen-deficient conditions at low temperatures (<500°C) (Lehmann, 2007). It is composed of carbonised organic matter (COM) and non-carbonised organic matter (NOM) (Chen et al., 2008) and from another point of view mineral and organic phase (Qian and Chen, 2013). This inorganic moieties (mineral part), COM and NOM fraction have been shown to play different roles on the sorption of contaminants. Chemo-thermal oxidation method (CTO-375) is a widely used method for soil/sediment PyC quantification by combusting soils under 375℃ to get rid of non-PyC (unstable) soil carbon (NOM). In this study, CTO-375 method was used to treat several commercial biochars to simulate the influence of wildfires (200℃ - 500℃) (Bornemann et al., 2007) on the sorption properties of biochars as wildfires are common in natural environment after biochar being introduced into soils. Cadmium (Cd), a carcinogenic element widespread in agricultural soils, is selected as a model contaminant in this study.

METHODS

In this study, biochars made from chicken manure (CM), green waste (GW), wheat chaff (WC) and trees chips (TC) by pyrolysis at 500 ℃ were purchased and sieved to 2 mm. After being combusted in a porcelain plate at 375 ± 2 ℃ for 24h under air atmosphere, the residues from several runs were collected and mixed to get enough homogeneous samples. Elemental analyses, BET surface area, porosity, scanning electron microscope (SEM) were used to characterise the original and treated chars (Char-Comb). H/C ratio (O+N)/C were calculated to evaluate aromaticity and polarity of these chars. Cd (II) adsorption experiment was performed using a batch equilibration technique by agitating 0.1g chars in 20 ml of 0.01 M $NaNO_3$ solution containing 2mM $Cd(NO_3)_2$ on a reciprocating shaker at 200 rpm for 24 h. Solution pH was recorded after equilibrium, and the mixtures were centrifuged, filtered through 0.22µm and acidified prior to Cd (II) measurement by ICP-OES. The sorbent residues were vacuum dried for further characterisation.

RESULTS AND DISCUSSION

The results indicated that except CM biochar, the combusted biochars all showed higher sorption capacity for Cd than their corresponding original biochars (Table 1). After combustion, Cd sorption capacity of WC char increased slightley, GW and TC biochars leaped around 4 times and 34.5 times, whereas that of CM char decreased by 67%. The reasons can be multiple.

Table 1: Characteristics of original and treated biochars, and their sorption for Cd

Samples	Properties					
	C	H/C	(O+N)/C	Surface area (m^2 g^{-1})	Equilibrium pH	Sorption capacity for Cd (mg kg^{-1})
GW char	60.92	0.05	0.59	1.09	5.73	3490
GW char-Comb	2.38	0.30	40.16	4.85	6.52	13946
CM char	41.53	0.05	1.31	3.56	6.52	32249
CM char-Comb	0.96	0.76	99.72	15.87	6.49	21295
WC char	52.03	0.07	0.83	1.66	6.40	20967
WC char-Comb	1.72	0.78	55.10	10.59	6.69	27645
TC char	68.70	0.04	0.39	2.12	6.44	1289
TC char-Comb	10.07	0.07	8.72	9.27	9.12	44527

(a) The pH of the combusted chars is higher than original chars except CM char. This increase in pH is likely to enhance Cd sorption.

(b) From the sharply dropped aromaticity (indicated by higher H/C ratio) and significantly increased polarity (showed by the soared (O+N)/C ratio), we can tell that organic fraction was mostly removed and the mineral phase became the main components for all biochars. As Cd (II) is a polar solute, these changes promoted the non-specific electrostatic sorption and may be precipitation of Cd (II) by forming Cd-mineral salt, indicating that mineral fraction of biochars can work better on Cd (II) sorption than all fractions working together.

(c) Meanwhile, surface areas of chars increased prominently due probably to the destruction of C skeleton and the piling up of finer mineral phase during combustion, providing more sorption surface sites for Cd (II) and enhanced its physical trap.

(d) As for CM biochar, enhanced sorption may be attributed to both the mineral as well as the organic fraction. Further work will be done to explore the sorption mechanisms underpinning these changes.

CONCLUSION

In summary:

(a) Mineral fraction was the major remaining fraction after combustion of biochars, indicating quite low COM fraction.

(b) Mineral fraction remaining showed higher sorption capacity for Cd (II) for three of the four biochars, implying that mineral fraction of these biochars plays an important role on the stabilisation of polar contaminants like Cd.

REFERENCE

BORNEMANN, L. C., KOOKANA, R. S. & WELP, G. 2007. Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. *Chemosphere,* 67**,** 1033-1042.

CHEN, B., ZHOU, D. & ZHU, L. 2008. Transitional Adsorption and Partition of Nonpolar and Polar Aromatic Contaminants by Biochars of Pine Needles with Different Pyrolytic Temperatures. *Environmental Science & Technology,* 42**,** 5137-5143.

LEHMANN, J. 2007. A handful of carbon. *Nature,* 447**,** 143-144.

QIAN, L. & CHEN, B. 2013. Dual Role of Biochars as Adsorbents for Aluminum: The Effects of Oxygen-Containing Organic Components and the Scattering of Silicate Particles. *Environmental Science & Technology,* 47**,** 8759-8768.

PHYSICO-CHEMICAL PROPERTIES OF BIOCHAR MADE FROM DIFFERENT SUBSTRATES

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INTRODUCTION

Biochar is a carbonaceous residue produced as a by product during the pyrolysis of carbon rich waste organic biomass. Biochar has gained significant attention in the past few years and is emerging as one of the suitable strategies for remediation of contaminated soils. The porous structure and negative surface charge of the biochar makes it a potential candidate for binding of heavy metal contaminants in the soil environment. As such, it can be utilised to mitigate the soil contamination and its transfer into the food chain.

Physico-chemical properties of the biochar vary and depend upon the source of biomass and pyrolysis conditions among other factors. A higher pyrolysis temperature generally leads to the increase in surface area of the biochar, which can facilitate the sorption of contaminants in the soil. This paper discusses (a) The production of biochar from different biomass (b) Physico-chemical properties of biochar.

METHODS

(a) Production of Biochar Samples

Eleven biochar samples were characterised in this study using the same pyrolysis process. The biochars were produced from hardwood pallets, wood chips, eucalyptus logs, pine offcuts, apple tree prunings, native scrub, barley straw, sawdust, pine off cuts, glory wine twigs and olive tree cuttings. All the biochars were produced using the same heating value of 48.9MJ/kg while the time for the completion of pyrolysis varied from 65 to 135 minutes. The maximum temperature achieved for the complete pyrolysis in all cases was from 340˚C to 685˚C. Carbon dioxide capturing efficiency of the biochars was in the range of 35-85%.

(b) Measurement of Physico Chemical Properties of Biochar

The physico chemical properties of the biochar were determined using established methods. Surface properties, in particular surface charge, of the biochar are the most important determinant in regards to their ability to potentially bind heavy metals in the soil. Electrochemical properties such as pH, electrical conductivity (EC), point of zero charge (PZC), Zeta Potential (ζ) were measured. Other properties like carbon, nitrogen content (CN) and elemental analysis of the biochar being studied were carried out as per methods available in the literature (Mohan et al. 2014; Yuan, Xu & Zhang 2011).

RESULTS AND DISCUSSION

(a) Biochar Yield and CN Analysis

The biochar yields were in the range of 41.38 - 61.34% wt. The carbon and nitrogen content observed for the biochar fall within the range of 46.83 – 77.97 % and 0.02 – 1.2 %.

(b) pH and Electrical Conductivity

All the biochar studied were alkaline in nature with pH ranging from 7.7 to 10.5. This is due to the presence of negative charge on the biochar. The electrical conductivity of the biochars studied was between 0.06 and 1.00 dSm^{-1}.

(c) Point of Zero Charge (PZC) and Zeta Potential (ζ)

The surface characteristics of the biochar are largely dependent upon the conditions of pyrolysis and the temperature achieved. Biochar with an acidic surface will attract negative species and the reverse happens when the biochar surface is alkaline in nature. The pH value at which biochar is devoid of any charge is referred to as point of zero charge (PZC). In the present study, the value of PZC found for most of the biochar was between 8 and 9 which corresponds with the values reported in the literature (Santos et al. 2015).

The presence of negative charges on the surface of the biochar is confirmed by the negative zeta potential values, which were measured by placing a known concentration of biochar-NaCl solution in an electric field of strength 10Vcm^{-1}.

CONCLUSIONS

The biochar from pyrolysis of eleven different biomasses are alkaline in nature. Pine offcuts biochar is the least alkaline with pH value 7.7 while apple tree pruning's shows high alkaline pH value of 10.5. Pyrolysis temperature and the type of feedstock biomass used are the main parameter affecting the characteristics of biochar. PZC and zeta potential values for all biochars indicate their potential in binding the heavy metal cations in the soil environment. The carbon content of the biochars suggests it can increase the carbon in the soil and overall soil quality of the soil can improve.

REFERENCES

Mohan, D, Kumar, H, Sarswat, A, Alexandre-Franco, M & Pittman Jr, CU 2014, 'Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars', *Chemical Engineering Journal,* vol. 236, no. 0, 1/15/, pp. 513-528.

Santos, L, Striebeck, M, Crespi, M, Ribeiro, C & De Julio, M 2015, 'Characterization of biochar of pine pellet', *Journal of Thermal Analysis and Calorimetry*, 2015/05/27, pp. 1-12.

Yuan, JH, Xu, RK & Zhang, H 2011, 'The forms of alkalis in the biochar produced from crop residues at different temperatures', *Bioresource Technology,* vol. 102, no. 3, pp. 3488-3497.

MODIFIED CYCLODEXTRIN EXTRACTION OF PHENANTHRENE IN BLACK CARBON AMENDED SOIL

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INTRODUCTION

Black carbon (BC) is a group of chemically heterogeneous carbon with exceptionally great sorptive capability. It was found to dramatically reduced biodegradability and chemical extractability of organic contaminants in soils. In the presence of > 0.1% BC, a well-established technique using hydroxylpropyl-β-cyclodextrin (HPCD) extraction to predict microbial degradability of organic contaminants in soils (Reid *et al.,* 2000) constantly underestimated mineralisation of phenanthrene (Rhodes *et al.,* 2008). It was suggested that water, as the solvent of aqueous HPCD solutions, was not capable of displacing phenanthrene molecules from BC particles.

With increasing release of BC into the environment, and its potential being a tool for contaminated land remediation, it is important to develop a reliable technique to assess the bioaccessibility of organic contaminants in soil (Semple *et al.,* 2013). For this purpose, a potential approach is enhancing the extractive capability of HPCD solutions by introducing a buffering system with higher pH to the solvent as Reid *et al.* (2000) identified greater extractive capability in HPCD solution prepared in phosphate buffer (pH 8).

This research aimed to test the effect of increasing pH on the extractive capability of HPCD solutions for phenanthrene in soil amended with different types of intentionally produced BC after different periods of soil-contaminant interactions.

METHODS

Pristine soil (A horizon; 5 – 20 cm) was collected from Myerscough Agricultural College in Lancashire, UK, and passed through a 2 mm sieve. Subsequently, 1% (dry weight basis) of three different BC (P3-1, BP2, CP2) were blended into the soil.

Both ^{12}C- and ^{14}C-phenanthrene was then spiked to the soil with about 1% (v/w) acetone as carrier. Stainless spoons were used to assist mixing and achieved final ^{12}C-phenanthrene concentration at 10 mg kg^{-1} and ^{14}C-associated radioactivity at 64 – 78 kBq kg^{-1} on dry weight basis. The spiked soil was then stored at room temperature (21 ± 1 °C) for 1 day (1 d) and 25 days (25 d) before used for extraction.

Extraction assays were conducted using HPCD solutions (60 mM) prepared in deionized water (pH 5.89), and phosphate buffers adjusted solutions at pH 7 and 8 following descriptions by Reid *et al.* (2000). Soil samples in triplicate (1.25 ± 0.1 g) from each treatment were weighed into 35 ml Teflon centrifuge tubes, and 25 ml of the HPCD solution was added. The tubes were then placed on an orbital shaker at 100 rpm for 22 h before centrifuged at 3600 rpm for 1 h. 5 ml supernatant was then sampled and mixed with 15 ml of Goldstar scintillation cocktail and analyzed with liquid scintillation counting (LSC) after storage in darkness for 12 h.

RESULTS AND DISCUSSION

Addition of 1% BC led substantial decrease (> 99%) in the extractable amount of phenanthrene regardless the type of BC as well as ageing period (Table 1). This observation reflected the extensive sorption of phenanthrene to BC, while the aqueous HPCD solution was not capable to disperse phenanthrene molecules from sorption on BC particles.

At both ageing time, HPCD in buffer of pH 7 extracted significantly higher ($p < 0.05$) amount of spiked phenanthrene (> 1%) from BC-treated soils compared to that extracted by non-adjusted aqueous HPCD solution (pH at 5.89) or buffer solution at pH 8 ($p < 0.05$). The amount of phenanthrene extracted by non-adjusted aqueous HPCD solution and HPCD buffer solution at pH 8 were not statistically different ($p > 0.05$). It seemed the introduction of phosphate buffers resulted in a biphasic effect on the extractive capability of HPCD solutions in BC amended soils.

Table 1. Total extent of ^{14}C-phenanthrene extracted by HPCD solutions from soils amended with 0% black carbon and 1% P3-1, CP2, and BP2 at 1 and 25 day soil-phenanthrene contact time. Errors are shown as 1 SEM ($n = 3$). Values in the same column followed by the same letter, or row followed by the same number are statistically similar (student t-test and ANOVA Tukey test, $n = 3$, $p < 0.05$).

Ageing period (days)	HPCD solution	Black carbon treatment			
		0% BC	1% P3-1	1% CP2	1% BP2
1 day	dH_2O	74.16 ± 0.39^{a1}	0.08 ± 0.08^{a2}	0.08 ± 0.02^{a2}	0.10 ± 0.10^{a2}
	pH 7	74.96 ± 0.80^{a1}	1.37 ± 0.07^{b2}	1.03 ± 0.21^{b3}	1.10 ± 0.14^{b3}
	pH 8	72.70 ± 1.46^{a1}	0.05 ± 0.05^{a2}	0.11 ± 0.08^{a2}	0.11 ± 0.11^{a2}
25 day	dH_2O	14.29 ± 1.05^{b1}	0.01 ± 0.01^{a2}	0.06 ± 0.06^{a2}	0.02 ± 0.02^{a2}
	pH 7	24.71 ± 1.35^{c1}	1.56 ± 0.17^{b2}	1.11 ± 0.09^{b3}	1.01 ± 0.17^{b3}
	pH 8	31.69 ± 0.06^{d1}	0.20 ± 0.12^{a2}	0.20 ± 0.13^{a2}	0.13 ± 0.10^{a2}

The buffered extracts from all soil treatments at each time point were highly coloured, indicating it had promoted dissolution of organic matter from soil (SOM). It is proposed that this effect would subsequently increase the solubility of phenanthrene by promoting partition it into the dissolved SOM. However, further increase of pH from 7 to 8 reduced the phenanthrene extractability. The underling science behind this might be the electrostatic attraction between the phenanthrene molecules (π electron donor) and SOM and BC.

It was explicitly demonstrated in this study that introduction of buffering systems with higher pH brought enhancement to extractive capability of HPCD solutions and it was a viable approach to modify HPCD extraction in presence of BC. It was proposed that further researches were needed to optimize this modification.

CONCLUSIONS

Introduction of buffering systems with higher pH is a valid approach to modify HPCD extraction to measure bioaccessibility of organic contaminants in soils amended with BC, provided further research into optimizing the process is carried out.

REFERENCES

Reid, B. J., Stokes, J. D., Jones, K. C., & Semple, K. T. (2000). Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. Environmental Science & Technology, 34(15), 3174-3179.

Rhodes, A. H., Carlin, A., & Semple, K. T. (2008). Impact of black carbon in the extraction and mineralization of phenanthrene in soil. Environmental Science & Technology, 42(3), 740-745.

Semple, K. T., Riding, M. J., McAllister, L. E., Sopena-Vazquez, F., & Bending, G. D. (2013). Impact of black carbon on the bioaccessibility of organic contaminants in soil. Journal of hazardous materials, 261, 808-816.

DISSOLVED ORGANIC MATTER, CHEMICAL SPECIATION AND PHYTOAVAILABILITY OF LEAD IN CONTAMINATED SOIL AMENDED WITH COMPOSTED AND UNCOMPOSTED ORGANIC MANURES

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INTRODUCTION

The use of organic amendments is gaining attention globally as a sustainable approach for restoration of contaminated sites (Fleming *et al*., 2013). However, the efficiency of this method depends on the composition of organic manure and the Dissolved Organic Matter (DOM) contents. DOM content of different organic amendments is the main factor determining their effectiveness and bioavailability of heavy metals in contaminated medium.

DOM can either increase the availability of metals (Li *et al*., 2012) or reduce it (Fleming *et al*., 2013)depending on its compositions and functional groups (Chefetz et al., 1998b; Salati *et al*., 2010). This in turn is determined by the kind of organic matrix and the maturity. Non-composted organic manure has been reported to contain higher amount of DOM than composted manure (Salati *et al*., 2010). On the other hand composting of organic manure has been reported to either increase or decrease the DOM of organic manure depending on the type of organic manure and composting duration (Chefetz *et al.,* 1998b). In this study, the effects of composting of cowdung, poultry manure and their combinations on the DOM, Pb speciation and bioavailability to plants were investigated.

METHODS

The experiments involved incubation and greenhouse studies using lead-contaminated soil.

Composting procedure and treatments

Cowdung and Poultry manure were composted separately and in combination using the Partially Aerated Composting Technique (PACT-2). Cowdung and poultry manure were laid out in ratio 2:1 on dry weight basis. Compost was also made from poultry manure and Mexican sunflower following the same procedure. The treatments include, Composted Cowdung (CCD), Uncomposted Cowdung (UCD), Composted Poultry Manure (CPM), Uncomposted Poultry Manure (UPM), Composted Poultry Manure and Cowdung (CPM&CD), Compost and Control

Incubation studies and Chemical analysis

Incubation study was carried out on the contaminated soil using four levels (10, 20, 30 and 40t/ha) of each treatment and replicated three times. At four weeks, soil samples were taken for chemical analysis. DOM was extracted according to the method described by Li *et al* (2012) using TOC Analyzer (TOC Vcph, Shimadzu, Japan). The sequential extraction procedure for Pb was carried out following the procedure of Jena *et al* (2013). The greenhouse experiment was also conducted for four weeks using maize as test crop. The Pb concentrations in the soil and plant digests were determined using inductively coupled plasma emission spectrometry (ICP–OES, Thermo-Fisher, iCAP, 6300 series).

RESULTS AND DISCUSSION

Composting increased the total DOM in cowdung while it was decreased in the poultry manure (Fig 1). Addition of organic amendments generally reduced Pb concentration in

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exchangeable fraction compared to control as previously reported (Fleming et al., 2013) with the highest application rate of composted and uncomposted organics being superior to the lower rates (Fig 2). The concentration of Pb in this fraction was found to be inversely correlated to the DOM content in the soil-organic mixtures with higher application rate of cowdung (UCD4 and CCD4) having the highest DOM content and lowest percentage Pb concentration in exchangeable fraction (Fig 3) which was contrary to the previous reports (Salati *et al.*, 2010). Meanwhile, only soil amended with both uncomposted cowdung and poultry manure as well as their combination at different rates supported maize growth. The Pb accumulation was however reduced at higher application rate (Fig 4).

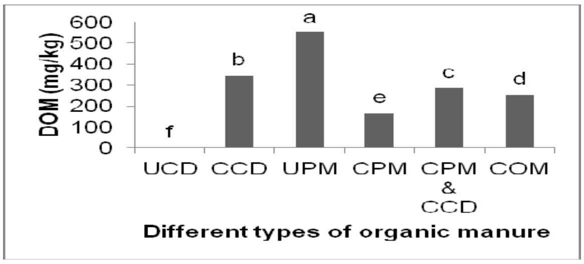

Fig. 1 **Effect of composting on Dissolved Organic Matter (DOM) content.**

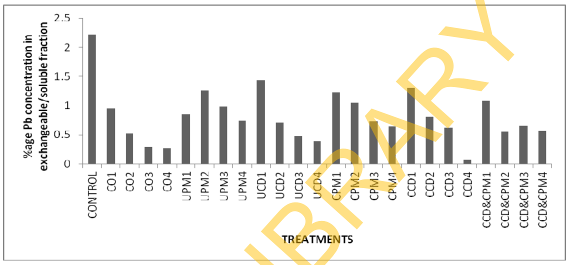

Fig. 2. **Percentage Pb concentration in exchangeable fraction.**

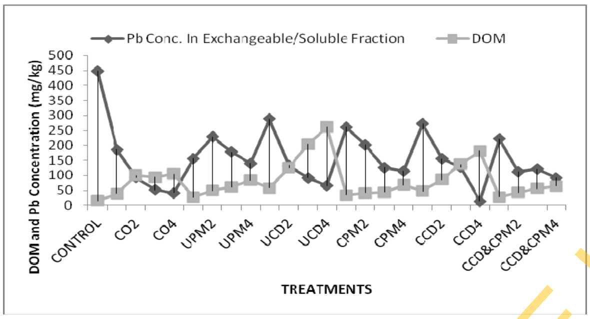

Fig. 3 **Relationship between Dissolved Organic Matter (DOM) content and Pb concentration in exchangeable fraction.**

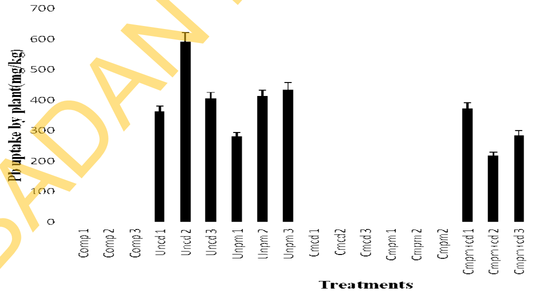

Fig. 4. **Effect of different rates of composted and uncomposted organic manures on Pb uptake by maize crop.**

CONCLUSIONS

Organic amendments reduced Pb concentration in exchangeable fraction and enhanced crop growth. Effect of composting on DOM concentration is based on the type of organic manure.

REFERENCES

Chefetz, B., Hadar, Y., Chen, Y., 1998b. Dissolved organic carbon fractions formed during composting of municipal solid waste: properties and significance. *Acta Hydrochimica et Hydrobiologica* 26 (3), 17 2–179.

Fleming Margaret, Tai Yiping, Zhuang Ping, McBride Murray B. 2013. Extrctability and bioavailability of Pb and As in historically Contaminated orchard soil: Effects of compost amendments. *Environmental Pollution* 177 :90-97

Jena V., Sapana G., Rakesh S., Natalija M, Stanislav F. and Neda D. (2013). Determination of total heavy metals by sequential extraction from soil. *International Journal of Research in Environmental Science and Technology* . 3(1) 35-38

Li T., Zhenghao X., Xuan H., Xiaoe Y., Donald L. (2012). Characterization of dissolved organic matter in the rhizosphere of hyperaccumulator Sedum alfredii and its effect on the mobility of zinc. *Chemosphere*. 88 (2012) 570–576.

Salati S., Quadri G., Tambone F., Adani F. (2010) Fresh organic matter of municipal solid waste enhances phytoextraction of heavy metals from contaminated soil. *Environmental Pollution* 158 (2010) 1899–1906.

COMPARATIVE STUDIES OF DIFFERENT SOIL REMEDIATING TECHNIQUES FOR LEAD CONTAMINATED SITE IN IBADAN, NIGERIA AND ITS EFFECT ON SEED GERMINATION AND CROP GROWTH

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INTRODUCTION

The health and environmental implications of soil contamination with heavy metals call for an effective technology to achieve a total clean up. Among contaminated soils however, those contaminated with heavy metals are said to be notorious and difficult to remediate. The remediation technologies commonly used are either mobilization to aid their removal from soil through complexation and solubilisation (Bolan *et al.,* 2010), or immobilization to decrease their mobility by reducing the bioavailable fractions in the soil through the use of soil ammendments (Adejumo *et al.,* 2011). However, based on the magnitude of contamination, different remediation technologies are sometimes used together to facilitate the remediation process. In this research work, effectiveness of three different methods (compost-remediation, soil mixing and soil washing) were assessed for remediation and enhancement of crop production on soil contaminated by lead-acid battery wastes.

METHODS

One of the abandoned lead-acid battery wastes dump-sites in Ibadan, Oyo State, Nigeria was used for the study. The soil on this site has been reported to contain high concentration of heavy metals especially lead (Pb: 124000 mg/kg)) thus making it unproductive and phytotoxic (Ogundiran and Osibamjo, 2008).

Experimental Procedure

Three experiments were carried out; Experiment 1 (compost remediation method using Mexican sunflower compost applied at two levels (40 and 50t/ha) and left for one month before planting (Adejumo *et al.,* 2011), Experiment II (Mixing of lead contaminated soil with uncontaminated soil in ratios; 25:75, 50:50, 75:25, 100:0 and 0:100 respectively to give five soil types and was later ammended with compost before planting, Experiment III (Initial soil washing with three types of solvent (Extractants; 2M Nitric acid, 10mM EDTA and distilled water) followed by compost ammendment. Soil washing was carried out by mixing soil with each extractant, and allowed to drain (Moon *et al.,* 2012). Thereafter the soils were rewashed twice with distilled water, allowed to dry and samples taken for analysis before compost addition and planting. Maize and Jathropha crops were used as test crops for the experiments. Soil Pb concentration was determined using 2M Nitric acid as described by Ogundiran and Osinbanjo (2008). The experiments were arranged using complete randomized design replicated 3times and percentage seed germination recorded.

RESULTS AND DISCUSSION

The soil was highly contaminated with Pb. Though, the result of chemical analysis showed that all the methods used (compost-remediation method, soil mixing with uncontaminated soil and soil washing) reduced the soil Pb concentration compared to control (100% contaminated soil) (Table 1) but, no germination was recorded in all the soil mixtures except the soil washed with 2M nitric acid and uncontaminated soil (0% contamination) with 96.00% and 66.30% germination and 85.00% and 65.00% germination recorded for both maize and Jatropha respectively (Table 2).. Again among the three extractants, 2M nitric acid reduced Pb concentration more than other extractants as was also observed by Moon *et al.* (2012).

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The results confirmed the previous findings that high concentrations of Pb caused decrease in germination and reduced the growth of seedlings (Pallavi and Dubey, 2005; Mesmar and Jaber, 2007). However, lack of germination probably could be due to osmotic stress induced by the high concentration of Pb salt in this soil thereby reducing water imbibitions by the seeds (Dkhil and Denden 2010). It was observed in the course of this experiment, that mixing of this contaminated soil with normal soil or compost enhanced the formation of white salt-like crystals whereas in the nitric acid washed soil no crystal was formed.

Table 1 . Lead concentrations in soil at one month after treatments

Treatments	C1	C2	S1	S2	S3	S4	S5	HN	ED	DW
Pb (mg/kg)	4606.5	4053.2	7560.0	7192.5	4762.7	63.0	16130.6	6967.7	9677.4	9935.5

S_1 = 75%, S_2 =50%, S_3 =25%, S_4 = 0%, S_5 = 100%,
C1 = 40t/ha Compost, C2= 60t/ha Compost ; HN =Nitric acid, ED= EDTA, DW= Distilled water

Table 2 . Effect of different treatments on seed germination

	Percentage germination									
Treatments	C1	C2	S1	S2	S3	S4	S5	HN	ED	DW
Maize	0.00	0.00	0.00	0.00	0.00	96.00	0.00	85.00	0.00	0.00
Jatropha	0.00	0.00	0.00	0.00	0.00	66.30	0.00	65.00	0,00	0.00

S_1 = 75%, S_2 =50%, S_3 =25%, S_4 = 0%, S_5 = 100%,
C1 = 40t/ha Compost, C2= 60t/ha Compost ; HN =Nitric acid, ED= EDTA, DW= Distilled water

CONCLUSIONS

It could be concluded that to achieve optimum remediation of heavy metal contaminated soil and enhance crop production, soil washing with nitric acid followed by compost addition could be employed

REFERENCES

Adejumo S.A., Togun A.O., Adediran J.A. and Ogundiran M.B, 2011. Field assessment of progressive remediation of soil contaminated with lead-acid battery waste in response to compost application. *pedologist*, 54(3):182-193

Bolan Nanthi, Naidu Ravi, Choppala Girish, Park Jinhee, Mora Maria Luz, Budianta Dedik and Panneerselvam Periyasamy. (2010). Solute Interactions in Soils in Relation to the Bioavailability and Environmental Remediation of Heavy Metals and Metalloids. *Pedologist,* Vol. 53 (3) pp 1-18

Dkhil Besma Ben and Denden Mounir (2010) Salt stress induced changes in germination, sugars, starch and enzyme of carbohydrate metabolism in *Abelmoschus esculentus* L. (Moench.) seeds *African Journal of Agricultural Research* Vol. 5(12), pp. 1412-1418

Mesmar M. N., Jaber K. (2007). The toxic effect of lead on seed germination, growth, chlorophyll and protein contents of wheat and lens. *J Environ Sci (China).* 19(6):725-32

Moon D. H., Lee Ju-Ry, Wazne M., Park J. (2012). Assessment of soil washing for Zn contaminated soils using various washing solutions. *Journal of Industrial and Engineering Chemistry*. Pp 18:822-825

Ogundiran M.B and Osibanjo O. (2008). Heavy metal concentrations in soils and accumulation in plants growing in a deserted slag dumpsite in Nigeria. *African Journal of Biotechnology.* Vol 21(2). Pp 59-69

Pallavi Sharma, Rama Shanke Dubey. (2005). Lead toxicity in plants. *Brazillan journal of plant physiology* 17;1677-2420

INSIGHTS INTO SOIL XRF DATA FROM THE NORTHAMPTON LEAD TAILINGS PROJECT

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INTRODUCTION

Phase 1 of the Northampton Lead Tailings Project (NLTP) focussed on screening some 700 properties for the presence of lead tailings historically used as fill throughout the town, including on residential properties. The lead tailings typically contain 2-3% lead (and variable concentrations of other heavy metals) which represent potentially unacceptable health risks to people who may be exposed to them or impacted soils (particularly young children). Whilst the lead tailings are visually distinct from natural soils and other fill types, field portable X-Ray Fluorescence (pXRF) devices were used to collect lead (and other associated heavy metals) concentration data to enable identification of properties with tailings and to make preliminary assessments of risks. Over 5,500 soil samples were collected over the course of the investigation and had pXRF measurements recorded to assist in identifying properties affected by tailings. The soils in Northampton are known to be naturally mineralised with lead and both tailings and natural soils are well graded materials. These are examples of factors which required some understanding to allow the pXRF data to be useful in achieving the study objectives. This presentation focuses on the data quality issues of the pXRF and the insights gained from the collection of a large dataset in terms of the quantitative assessment applied for the purpose of achieving the study's objectives. Note that other qualitative lines of evidence were also applied during the project.

METHODS

An initial pXRF data collection method was developed which included relatively simple sample preparation and multiple pXRF readings. Niton XL2 pXRF devices were subject to daily system checks and control sample measurements. Between 5-20 samples were collected from each property (depending on observations of soils, tailings and fill materials, the size and use of the property), placed into plastic sample jars and compacted by hand. The internal data logger on the pXRF was used to record the identification and nature of the sample before five 10 second readings were conducted. The raw total concentration data, average data and measurement error data were uploaded daily into a relational database specifically developed for the study.

Selected samples were also subjected to laboratory analysis using the standard environmental method for metals (method USEPA 3051A to determined acid digestible metals) for the purpose of evaluating whether the pXRF data were sufficiently reliable for identifying soils which may pose potentially unacceptable health risks. It was recognised that the pXRF instruments estimated total metals concentrations whereas the analytical procedures typically used for contaminated sites assessment measured acid digestible lead after removing the >2 mm fraction. This systematic difference was considered when comparing pXRF measurements to laboratory data and assessment criteria.

The pXRF sampling and analytical methodology was refined following an initial comparative assessment and further consideration of the nature of soils and the sample preparation processes. The principal refinements included the sieving and mixing of samples to reduce effects of grainsize and mineralogical heterogeneity (i.e. homogenise the sample) prior to pXRF measurement and use of a hot (260◦C) four acid digest laboratory analytical method. A second comparative assessment was undertaken to evaluate the refinements.

RESULTS AND DISCUSSION

As assessment of potential health risks and decisions for every property in the study included a quantitative assessment using pXRF data and lead was found to be the most significant

COPC in terms of possible risks, the data quality evaluation focused on lead concentration data as measured by pXRF.

In an initial comparative assessment between pXRF and laboratory data, the correlation between averaged pXRF data and laboratory data was strong for the whole dataset (R^2=0.88) but very weak for data in the 200-400 ppm lead concentration range (R^2=0.07). Relative Percentage Differences (RPDs) for lead concentrations in sample pairs were calculated, with 54% of RPDs greater than 30% the level considered elevated and indicative of less than adequate precision. Further examination of the results also found that there was a generally better and acceptable level of agreement when considering the ranges of pXRF data for samples.

Sample heterogeneity and the laboratory's use of an acid digestible metal analysis were identified as the most significant contributors to the variability which could be addressed, so trials were undertaken to consider changes to pXRF methodology. The trials indicated that the most significant changes were likely to be removal of >2 mm fraction before pXRF measurements and the laboratory utilising a totals metals analysis.

Re-evaluation of pXRF and laboratory data collected using the amended methodologies demonstrated an improvement in the level of agreement between the pXRF and laboratory data. The correlation coefficient between pXRF and laboratory lead concentrations (200-400 ppm) was 0.25 compared to the previous coefficient of 0.07. The improvement was accompanied with a reduction in the percentage of sample pairs with elevated RPDs (34% compared to 54% previously) and improved precision from repeat pXRF measurements (8% of RPDs elevated RPDs compared to 50% of RPDs elevated previously). These results also provided greater confidence that the pXRF measurements of lead concentrations were greater than the laboratory derived results and were therefore suitable for assessing lead concentrations and making decisions on affected soils and properties which were appropriately cautious for the investigation's objectives.

It was recommended that for future collection of lead concentration data in Northampton soils (i.e. during validation of remediation works) the refined methodology be employed. Specifically, samples subject to pXRF measurements are to be first sieved to remove the >2 mm fraction and laboratory analysis is to involve a four acid digest total concentration method. It was considered that several factors continued to contribute to variability between pXRF and laboratory data. For example, further homogenisation of samples by milling to 75 µm may further reduce grainsize effects, however given the improved level of agreement between the field and laboratory methods, this is not considered to be a worthwhile exercise for large numbers of samples (as expected in Phase 2).

CONCLUSIONS

The use of the pXRF devices allowed for a very large amount of data to be collected relatively quickly, easily and cheaply in comparison to traditional laboratory analytical data. The quality of pXRF data was evaluated closely and considered to be adequate for achieving the objectives of the Phase 1 of the NLTP. Physical and chemical heterogeneity of samples were identified to be the principal factors most affecting precision of pXRF data. Sample heterogeneity was reduced in the later stages of investigation by sieving and mixing of the samples prior to measurement, demonstrated by improved precision in pXRF measurements. The pXRF devices will likely prove useful again during remediation of tailings as they can provide real time validation results which can be considered reliable and defensible for the purpose of assessing human health risks.

Before the pXRF methodology can be widely adopted and accepted by the regulators as a technique for contaminated sites assessment, further consideration is required of the standard laboratory procedures for metals determination and the relationship between analytical techniques and field assessment criteria. There must also be a wider understanding on the benefits and limitations of pXRF data throughout the contaminated sites assessment community.

WATER MANAGEMENT PRACTICES IMPACT ARSENIC UPTAKE AND YIELD IN RICE

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ABSTRACT

Bioaccumulation of arsenic in rice grain that can impact human health including cancer has been identified as a serious public health issue in Bangladesh. A field study was conducted to investigate whether water management impacts the accumulation of arsenic within the rice grain in different rice cultivars. Ten common rice cultivars widely cultivated in Bangladesh were tested for susceptibility to arsenic under different irrigation options. Total grain arsenic accumulation was higher in the plants grown in high soil arsenic in combination with conventional irrigation practice. Results showed that appropriate water management practice and variety resulted in a reduction of grain arsenic level around 39% in addition to increase grain yield around 32%.

INTRODUCTION

Arsenic (As) intake from rice represents an important route of exposure for human, especially for people consuming large amounts of rice in their diet. Paddy rice is more efficient in As uptake than other cereal crops (Williams et al., 2007). Rice grown under flooded conditions was found to accumulate much more As than that grown under aerobic condition and this difference was attributed to the higher bioavailability of As in flooded soils (Williams et al., 2007). A significant genetic variability was also found among the cultivars for grain As bioaccumulation. In Bangladesh, As-contaminated water extracted through shallow tube-wells is widely used to irrigate rice crops during the dry season (Saha and Ali, 2007), which has resulted in elevated As concentrations in soils and rice grains, and significant yield losses due to As phytotoxicity (Khan et al., 2009, Panaullah et al., 2009). Water management techniques and rice cultivars dramatically affect the As concentrations in rice grains. Selecting appropriate irrigation practice and rice cultivars in As contaminated soils will benefit yields and low As in grain.

METHODS

A field experiment was carried out using eight of the most popularly grown Bangladesh Rice Research Institute (BRRI), Bangladesh Institute of Nuclear Agriculture (BINA) developed and two local brown rice cultivars at highly As contaminated soils of Faridpur district in Bangladesh, during the winter season (January-May) of 2014 with four replicates. Rice varieties tested were local, high yielding and aromatic. Two water management options i.e. continuous flooding (CF) and alternate wetting drying (AWD) were followed. Each plot had received recommended dosed of N, P, K and S fertilizers. The soil was clay loam in texture, having pH 7.6, organic matter 1.98%, total N 0.13% , available P 13.7 mg kg^{-1}, available S 13.7 mg kg^{-1}, exchangeable K 0.11 meq 100g^{-1}, cation exchange capacity 10.1 me 100g^{-1} soil and total As 15.69 mg kg^{-1}.

Sample Digestion and Analysis

Concentrated nitric acid (PrimarPlus-Trace analysis grade, UK) was used for the digestion of the rice samples by the procedure of Rahman et al. (2009). An Agilent 7500ce inductively

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coupled plasma mass spectrometry (ICP-MS) was used for the determination of As in digested rice grain samples. Trace elements in rice flour (SRM 1568a) from the National Institute of Standard and Technology (NIST), USA was used to verify the analytical results for As. For As speciation, rice samples were extracted with 2 M tri-fluoacetic acid (TFA).

RESULTS AND DISCUSSION

Arsenic contamination reduced grain and straw yields of rice. There was a significant ($p<0.05$) difference in grain yield shown among the cultivars under the CF and AWD irrigation practices. Alternate wetting and drying irrigation treatment significantly increased grain yields over CF practice and around 32% yield difference. The variety with the highest yields was BRRI dhan58 followed by BRRI dhan47, BINA dhan10 and BINA dhan8.

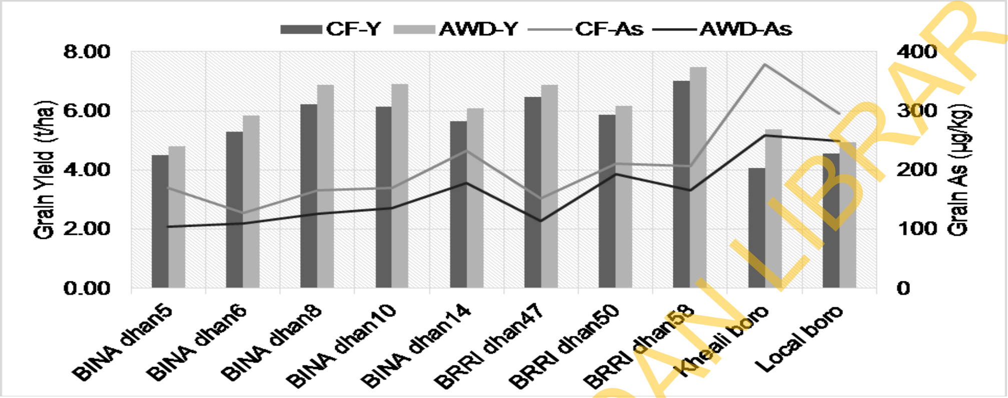

Fig.1. Grain yield and As conc. in different cultivars under CF and AWD irrigation practices.

There was also a significant ($p<0.05$) difference in grain As concentrations between cultivars and water management. Arsenic concentrations in different rice varieties were markedly higher in the CF treatments than in the AWD treatments. Overall, there was a 20 to 39% difference in grain As concentrations between the CF and AWD irrigation practices among the rice cultivars. Speciation of grain As were found not to differ among the varieties in respect to inorganic As around 88 to 98%.

CONCLUSIONS

This study demonstrates that irrigation option AWD not only to significantly increase rice grain yields in rice, but also to reduce the concentration of As in rice.

REFERENCES

KHAN, M. A., ISLAM, M. R., PANAULLAH, G. M., DUXBURY, J., JAHIRUDDIN, M. & LOEPPERT, R. 2009. Fate of irrigation-water arsenic in rice soils of Bangladesh. *Plant and Soil,* 322**,** 263-277.

PANAULLAH, G., ALAM, T., HOSSAIN, M. B., LOEPPERT, R., LAUREN, J., MEISNER, C., AHMED, Z. & DUXBURY, J. 2009. Arsenic toxicity to rice (Oryza sativa L.) in Bangladesh. *Plant and Soil,* 317**,** 31-39.

RAHMAN, M., OWENS, G. & NAIDU, R. 2009. Arsenic levels in rice grain and assessment of daily dietary intake of arsenic from rice in arsenic-contaminated regions of Bangladesh—implications to groundwater irrigation. *Environmental Geochemistry and Health,* 31**,** 179-187.

SAHA, G. C. & ALI, M. A. 2007. Dynamics of arsenic in agricultural soils irrigated with arsenic contaminated groundwater in Bangladesh. *Science of The Total Environment,* 379**,** 180-189.

WILLIAMS, P. N., VILLADA, A., DEACON, C., RAAB, A., FIGUEROLA, J., GREEN, A. J., FELDMANN, J. & MEHARG, A. A. 2007. Greatly Enhanced Arsenic Shoot Assimilation in Rice Leads to Elevated Grain Levels Compared to Wheat and Barley. *Environmental Science & Technology,* 41**,** 6854-6859.

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ECOTOXICITY ASSESSMENT OF HEAVY METALS- AND DIESEL-CONTAMINATED SOILS

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INTRODUCTION

Various remediation techniques have been applied to remove contaminants such as heavy metals and diesel from soil environments. However, the evaluation of residual toxicity after remediation action is one of the important issues in the assessment of soil quality. In order to determine the risk of contaminated and remediated soils, chemical analyses need to be complemented with biological and toxicological approaches. The objectives of this study were to assess the ecotoxicity of soils co-contaminated with heavy metals and diesel using a battery of bioassays representing different trophic levels and to investigate the effects of remediation action on the ecotoxicity.

METHODS

Contaminated soil remediation process was performed by In-situ soil mixing/flushing technique on railroad site. Ecotoxicity tests were performed using both soil samples as the before and after remediation. The biomass change of earthworm (*Eisenia fetida*), germination rate and growth of tomato (*Lycopersicon esculentum*) were examined the effects on soil invertebrate and plant using soil as test medium. Soil elutriates were extracted to perform the inhibition of bioluminescence with photobacterium (*Vibrio fischeri*), and an immobilization bioassay with *Daphnia magna*.

RESULTS AND DISCUSSION

The concentration of TPH in the soil decreased by 77% after remediation, and concentration was significantly reduced in the case of heavy metals. The observed toxicity of earthworm and tomato increased, depending on the content of the contaminated soil. However, toxic effect did not correlate with the before/after remediation soil. Both eluates of before and after remediation soils showed no toxic effects on *Vibrio fischeri* and *Daphnia magna*.

CONCLUSIONS

In this study environmental toxicity tests were compared for before and after remediation soils originated form railroad site. The concentration of pollutants decreased during remediation. The results of ecotoxicity tests correlated only the content of the contaminated soil. However, the value of the soil ecotoxicity increased after remediation. These results show that the remediation processes used to clean contaminated soil also changing soil properties (pH, organic content, etc.) and loss soil nutrients. To utilize the cleaned soil for healthy and more value-added purposes, soil improvement and process development are needed.

ACKNOWLEDGEMENT

This research is financially supported by Republic of Korea Ministry of Environment as "Green Remediation Research Center for Organic-Inorganic Combined Contamination (The GAIA Project-2012000550001)".

REFERENCES

Gong, X.B. (2012) Remediation of weathered petroleum oil-contaminated soil using a combination of biostimulation and modified Fenton oxidation. Int. Biodeterior. Biodegradation. 70:89-95.

Płaza, G., Nałecz-Jawecki, G., Ulfig, K. and Brigmon, R.L. (2005) The application of bioassays as indicators of petroleum-contaminated soil remediation. Chemosphere. 59:289-296

Santorufo, L., Van Gestel, C.A. and Maisto, G. (2012) Ecotoxicological assessment of metal-polluted urban soils using bioassays with three soil invertebrates. Chemosphere. 88:418-425

BACKGROUND CONCENTRATIONS OF HEAVY METALS IN THE NEWER VOLCANICS AQUIFER WITHIN THE MELBOURNE AREA

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INTRODUCTION

The Newer Volcanics basalts cover an area of 19,000 km^2 that extends westwards from central Victoria into South Australia, and were erupted from the Late Miocene (~4.5 Ma) to the Holocene (~5 ka) (Boyce, 2013). The Newer Volcanics Aquifer is predominantly unconfined with a low fracture porosity (~5%). Clay-rich soil horizons within and overlying the aquifer act as leaky aquitards. The groundwater within the aquifer provides baseflow to surface waterways and also discharges into Port Phillip Bay (Finegan, 1996).

The aim of this research was to ascertain the background concentrations of heavy metals within the Newer Volcanics Aquifer groundwater, to determine if these naturally exceed the national water guidelines, without the presence of contamination.

METHODS

Geological and groundwater maps for the Melbourne area delineated the area covered by the Newer Volcanics Aquifer. The EPA Victoria Environmental auditing database for Issued Certificates and Statements of Environmental Audit was used to search for environmental audit reports within this area (EPA Victoria, 2013). Only reports with basalt groundwater analyses and no history of contamination in the groundwater were selected. The data from each of the reports was combined and analysed in Microsoft Excel, using, firstly, only analytical results greater than Limit of Reporting (LOR) values, and secondly, all data (for results <LOR, a value half of the LOR value was used). The median concentrations for each heavy metal (obtained using both methods) were compared to a range of national water guidelines, as well as the metal concentrations within the basalt aquifer (Price et al. (2003).

RESULTS AND DISCUSSION

The concentrations of heavy metals in some basalt groundwaters exceed the national guidelines (Fig 1). In particular, >70% of chromium and copper analyses, both with and without LOR values, exceed ANZECC freshwater guidelines. However, the guideline values for Cr refer to hexavalent Cr only, whereas the analyses are for total Cr, including Cr(III) which is not considered to be an environmental contaminant. Lead, nickel and zinc analyses all exceeded the freshwater ecosystem guidelines in more than 50% of bores.

Comparing the median groundwater metal concentrations with the concentrations of metals in the basalt aquifer (Figure 2) shows a strong positive correlation, indicating that these metals are derived from the basalt and represent natural background levels in this aquifer. The comparatively higher concentration of barium in the groundwater reflects its higher mobility relative to the other metals.

CONCLUSIONS

Within the Melbourne area of the Newer Volcanics Aquifer, the heavy metal concentrations in the groundwater often exceed national guideline values. These high concentrations are naturally occurring, due to leaching of the metals from the surrounding basalt.

ACKNOWLEDGEMENTS

This project was supported by the ACLCA collaborative research committee.

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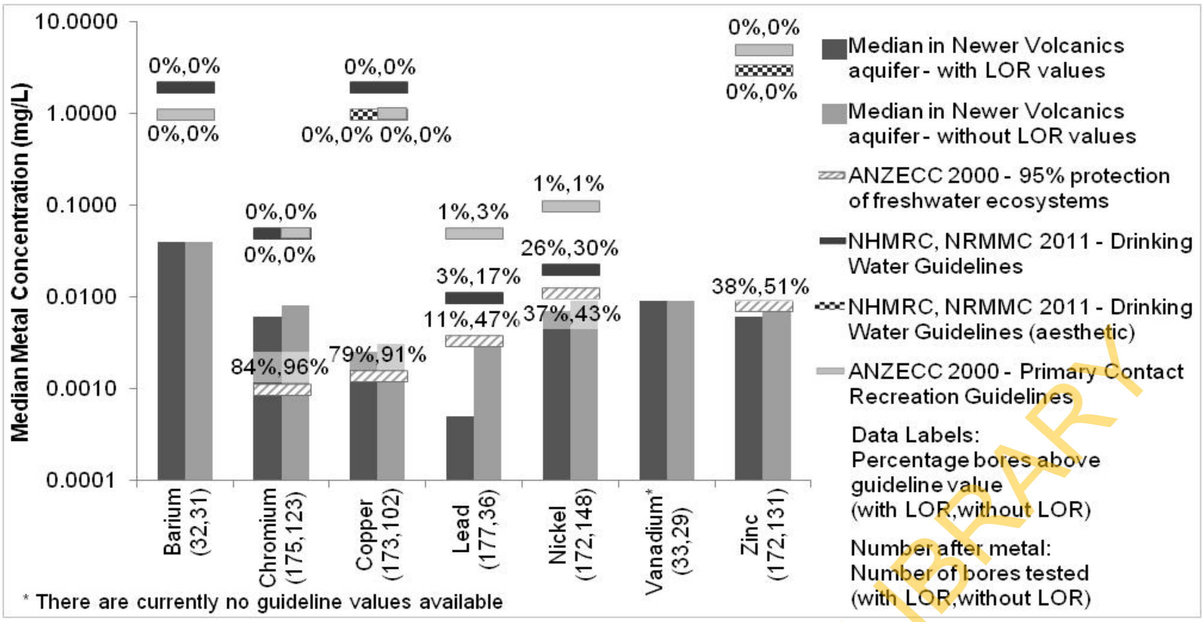

Fig. 1. The percentage of groundwater samples naturally exceeding the allowable metal concentrations in the NHMRC Drinking Water Guidelines and ANZECC Guidelines (ANZECC & ARMCANZ, 2000, NHMRC, NRMMC, 2011).

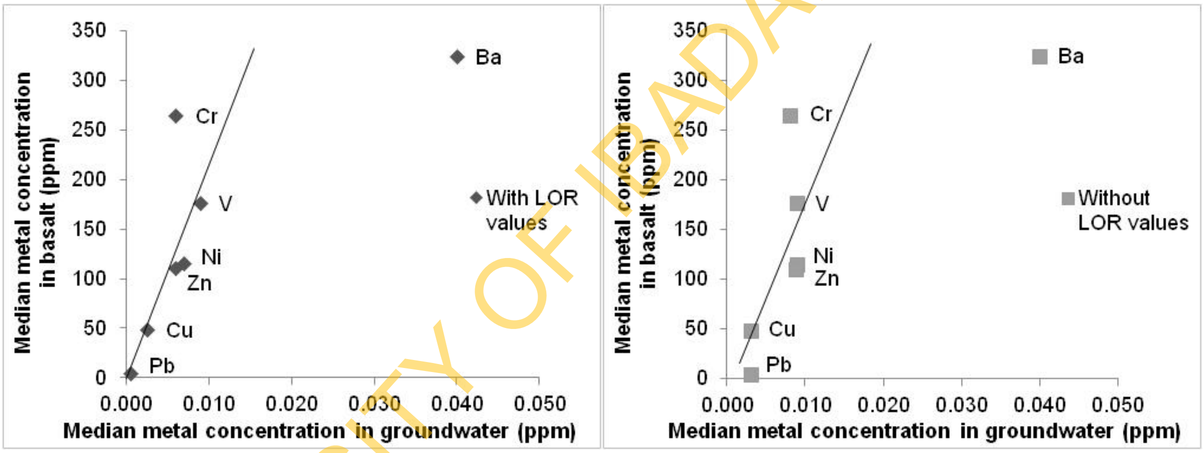

Fig. 2. Comparison of median metal concentrations in the Newer Volcanics basalt and groundwater.

REFERENCES

ANZECC & ARMCANZ (2000) Australian and New Zealand guidelines for fresh and marine water quality. National water quality management strategy paper.

Boyce, J. (2013) The Newer Volcanics Province of southeastern Australia. Australian Journal of Earth Sciences, 60, 449-462.

EPA Victoria (2013) Issued certificates and statements of environmental audit. Victoria: State Government of Victoria.

Finegan, J. M. (1996) Transport, attenuation, and degradation of organic chemicals in a basaltic aquifer system near Melbourne, Australia. PhD Thesis. The University of Melbourne. Melbourne, Australia.

NHMRC, NRMMC (2011) Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.

Price, R., Nicholls, I. & Gray, C. (2003) Cainozoic igneous activity. *In*:Birch W.D. ed. *Geology of Victoria*, pp. 361–375. Geological Society of Australia Special Publication **23**.

CADMIUM SOLUBILITY AND PLANT UPTAKE IN CONTAMINATED SOIL: VALIDATED TRANSFER FUNCTIONS

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INTRODUCTION

Cadmium is heavy metal that is of considerable concern in the environment. In soils, Cd is found at typically low concentrations (approx. <0.5 mg kg-1), but even a relatively small loading of agricultural soil with Cd from fertilizers has raised concern for human health. Translocation to agricultural crops is of concern to human health; likewise translocation to edible parts of plants is of concern for mammalian toxicity and food chain transfer. Cadmium solubility and uptake from soil solution is a function of solid and solution properties. The ability to provide predictive models for solubility and transfer to various trophic levels in the food chain is important in the management of Cd in agricultural and contaminated soils. In this study, we determined Cd partitioning constants for a 41 soils from across Australia in order to examine the role of soil properties controlling Cd partitioning. We also investigated the ability to predict Cd partitioning from multivariate regression models. From a series of sorption studies and dose response relationships we developed transfer functions predicting Cd solubility and uptake in *Cucumis sativa L*. The dataset was validated with 15 long-term contaminated soils ranging in Cd concentration from 0.2 to 300 mg/kg.

METHODS

Forty-one uncontaminated soils were sampled with contrasting soil properties from across Australia. Cadmium sorption isotherms were performed for each soil.

Dose response study

Ten soils were selected and spiked with cadmium nitrate up to 1000 mg Cd/kg and incubated for 4 months at below field capacity. Phytotoxicity and accumulation was studied in a 4 week pot study. Cadmium solubility was studied in each soil and speciation calculated from pore-water analysis using WHAM 7 model.

Validation dataset

To validate Cd solubility and uptake 15 soil samples enriched in Cd from smelter out fall were sampled. The same process used for the dose response study was applied to the validation set. All statistical analysis was performed using the statistical software package SPSS (SPSS, version 17, Chicago, Illinois). All parameters except pH was used as log10 values.

RESULTS AND DISCUSSION

Soil properties used for model development varied widely (Table 1). The Freundlich partition coefficient (K_f) ranged from 0.460 to 1286 l kg^{-1}. The parameter log K_f was predicted extremely well with soil pH_s and logCEC, log OC and both logCEC and log OC (RMSE <0.5). The estimated regression paramters for log K_f were quantitatively comparable to Sauve et al. (2000). Cadmium phytotoxicity was modelled for all 10 soils using Cd^{2+} and Cd_{pore}, although considerable variation existed. Dose-response curves indicated that Cd^{2+}, and Cd_{pore} and Cd_{shoot} concentrations relating to a 10% reduction in cucumber growth was 0.03 µ*M*, 0.37 µ*M* and 8.7 mg kg^{-1}, respectively. The best model for predicting Cd_{pore} was: $\log[Cd]_{pore}$ = 0.698

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+0.689logCd_{total} – 0.891logK_f. This model was applied to the validating set of smelter soils. The series of equations predicting K_f, Cd_{pore} and Cd_{shoot} were able to successfully predict the measured data in the independent dataset with RMSE values of 1.44 for Cd_{pore} and 0.32 for Cd_{shoot} (Figure 1).

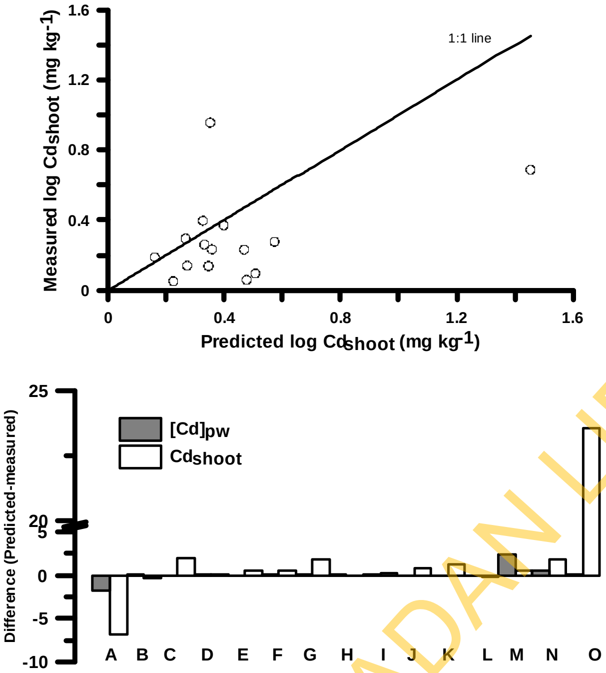

Figure 1. Comparison of modelled Cd from validating soil dataset. Top shows the relationship between predicted Cd_{shoot} and measured (log). Bottom graph shows quantitative differences between predicted and measured concentrations of Cd_{pw} (µ*M*) and in shoot (mg kg^{-1}) for the validating set of smelter impacted soils (predicted-measured). RMSE Cd_{pw} = 1.44; Cd_{shoot} = 0.32.

Table 1. Summary of soil properties used for model development, including soil pH, OC, Clay, CEC, acid-oxalate extractable Fe oxide (Feox), water-extractable Cl^-, the Freundlich partition coefficient (K_f) and associated R^2 for each soil.

	pHs	OC %	Clay %	CEC cmol kg^{-1}	Fe_{ox} g kg^{-1}	Cl mg kg^{-1}	K_f L kg^{-1}	R^2
min	2.96	0.01	2.6	0.5	<bdl	<bdl	0.460	0.84
max	8.3	10.6	62.3	48.7	9.51	912.8	1286	1.00
median	5.58	2.76	18.5	9.9	1.47	25.19	68.39	0.99
Mean	5.79	2.87	26.1	13.2	2.58	122.1	269.4	0.97
SD	1.42	2.30	19.5	12.1	3.05	241.7	381.4	0.04
Skewness	0.2	1.7	0.95	1.7	2.1	2.7	1.6	-2.4
N	41	41	40	41	41	40	41	41

REFERENCES

Sauvé, S., Hendershot, W., & Allen, H. E. (2000). Solid-Solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter. *Environmental Science & Technology, 34*(7), 1125-1131. doi: 10.1021/es9907764

REMOVAL OF HEXAVALENT CHROMIUM USING GREEN SYNTHETIC AGAROSE-Fe NPs HYDROGEL BEAD

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INTRODUCTION

Hexavalent chromium (Cr(VI)) contamination has been increasingly aroused extensive attention because of its toxicity, carcinogenicity, mutagenicity, and teratogenicity (Fendorf et al., 2000, Norseth, 1980). Considering these properties and non-biodegradation, Cr(VI) must be physically or chemically removed from contaminated water before being discharged into aquatic system. Conventional methods have some drawbacks, such as the cost is relatively high (Mohan et al., 2005). Consequently, it is still necessary to develop novel efficient and cost-effective remediation strategies. Fe nanoparticles (NPs) have been documented to work efficiently in environmental remediation area both in soils and wastewater due to their easy accessibility and high degradation rate. However, there are still some challenges associated with practical applications. Specifically: (1) Fe NPs are easy to agglomerate in water to form larger aggregates due to magnetic and van der Waals forces or to react with air, contributing to the significant loss of reactivity; (2) Conventional synthesis approaches for the production of Fe NPs have some drawbacks, making site remediation become an unwanted financial burden and as such environmental technologies typically exhibit a relatively low market value; (3) Fe NPs are highly mobile in the aquifer and it is extremely difficult to recycle the dispersed Fe NPs from wastewater. Our latest study was concentrated on developing novel technology to immobilize green synthetic Fe NPs and then applied into the environmental remediation.

METHODS

In this study, green synthetic Fe NPs were firstly immobilized using agarose in the form of hydrogel bead for application in environmental remediation. Specific contents include:

(a) The synthetic method for Fe NPs is the same as described in our previous study (Luo et al., 2014). To obtain agarose-Fe NPs hydrogel bead, heating the agarose solution which was prepared by adding 0.075 g of agarose in 6 mL of water until agarose was completely dissolved on the stirrer. Then, 0.080 g of Fe NPs was added into the hot agarose solution. The agarose-Fe NPs solution was then dropped into the liquid nitrogen by pipette tip and the hydrogel beads were formed immediately.

(b) Scanning electron microscopy (SEM) was performed to characterize the morphology of agarose-Fe NPs hydrogel bead.

(c) To validate whether agarose-Fe NPs hydrogel perform equally well as bare Fe NPs, a comparative assay on the removal efficiency of Cr(VI) using agarose-Fe NPs hydrogel and bare Fe NPs was investigated under the same conditions.

(d) X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were used to identify the mechanisms.

RESULTS AND DISCUSSION

(a) Fig.1a showed that the fresh synthesized agarose-Fe NPs hydrogel beads were generally spherical and black in colour and the average diameter was around 5 mm.

SEM image (Fig.1b) clearly revealed that the centre of agarose-Fe NPs hydrogel was porous.

(b) Comparative assay (Fig.1c) showed that approximately 96.7% of Cr(VI) was removed by agarose-Fe NPs hydrogel within 24 h, which was slightly higher than that using bare Fe NPs (around 94.5%). This result demonstrated that agarose-Fe NPs hydrogel performed comparably to bare Fe NPs with little change in their reactivity.

(c) Results of XPS and FTIR demonstrated that Cr( ) and some iron oxides were appeared after the removal process.

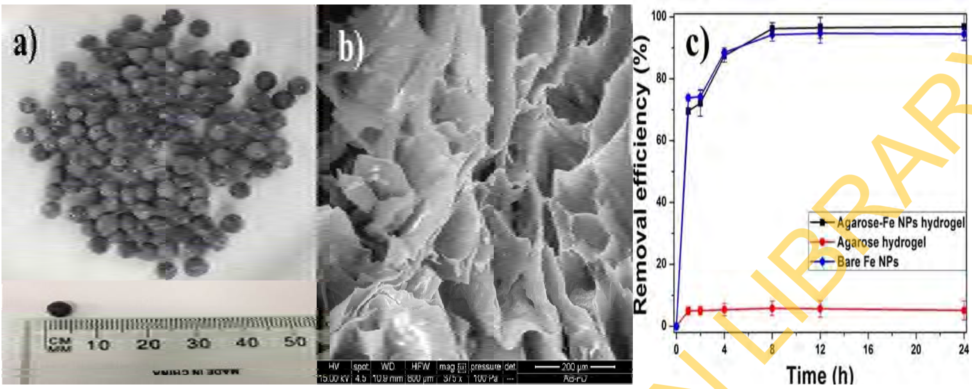

Fig.1 a) The freshly synthesized agarose-Fe NPs hydrogel bead; b) SEM image for the centre of dried agarose-Fe NPs hydrogel bead; c) Removal efficiency of Cr(VI) using agarose-Fe NPs hydrogel, bare Fe NPs and agarose hydrogel.

CONCLUSION

We reported a simple green synthetic method for the preparation of agarose-Fe NPs hydrogel bead. This hydrogel was nontoxic, biodegradable and biocompatible. SEM clearly showed that the centre of agarose-Fe NPs hydrogel was porous and the porosity allowed solutes diffuse into the beads and come into contact with the immobilized Fe NPs, which ensured agarose-Fe NPs hydrogel work equally well as the bare Fe NPs. Results of XPS and FTIR confirmed that adsorption and reduction may be both involved in this removal process.

ACKNOWLEDGEMENT

Part of this project was financially supported by the CRC for Contamination Assessment and Remediation of Environment (Project: 4.1.6-11/12), Australia. Miss Fang Luo is supported by the International Postgraduate Research Scholarship (IPRS) program.

REFERENCES

FENDORF, S., WIELINGA, B. W. & HANSEL, C. M. 2000. Chromium transformations in natural environments: the role of biological and abiological processes in chromium (VI) reduction. *International Geology Review,* 42, 691-701.

LUO, F., CHEN, Z., MEGHARAJ, M. & NAIDU, R. 2014. Biomolecules in grape leaf extract involved in one-step synthesis of iron-based nanoparticles. *RSC Adv.,* 4, 53467-53474.

MOHAN, D., SINGH, K. P. & SINGH, V. K. 2005. Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. *Industrial & Engineering Chemistry Research,* 44, 1027-1042.

NORSETH, T. 1980. Cancer hazards caused by nickel and chromium exposure. *Journal of Toxicology and Environmental Health, Part A Current Issues,* 6, 1219-1227.

EVALUATION OF ORGANIC-INORGANIC MIXTURE TOXICITY IN COMBINED CONTAMINATED SOIL

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INTRODUCTION

Co-contaminated subsurface remediation has been reported in many parts of the world. According to previous studies, there is significant difference in biodegradation between single and combined contamination due to the different toxicities of contaminants (Suja et al., 2009). Therefore, it is important to understand the toxic effects in co-contaminated soils. There are several assays to detect the mutagenicty/genotoxicity in soil environment. Ames and Microtox^{TM} are the most widely used assays among these. In this study, we evaluated the mixture toxicity on indigenous microorganisms in organic and inorganic-combined contaminated soils and investigated the correlation between the Ames and Microtox^{TM} test.

METHODS

Ames test

The toxic and mutagenic effects of extracts from organic and inorganic-combined contaminated soils were tested over a range of concentrations to determine the dose-related mutagenic response curve for each compound. Soil extracts from organic and inorganic-combined contaminated soils were tested for mutagenicity at different dilutions. After 1g of soils were extracted with dichloromethane (DCM), aliquots of the DCM extract (0.1 to 2.0mL) were dried under a gentle stream of nitrogen and resuspended in 0.1mL dimethylformamide (DMF). Each soil extract and strain combination was poured in five replicate plates. Negative controls, containing combinations of the tester strain, S9, and DMF without soil extract, were prepared to estimate the number of revertants from spontaneous mutation. The plates were incubated at 37°C for 48h before counting revertants.

Microtox^{TM} test

Soil samples (5g, wet weight) were diluted in deionized water (20mL) and shaken at 200 rpm for 2h at 22°C. They were allowed to settle and centrifuged for 15min at 3000rpm. The salinity of the supernatant was adjusted to 3% (w/v) by adding NaCl. An overnight culture of the indigenous microorganisms was prepared in proteose peptone (PP) medium at 24°C. Toxicity assays were performed by adding the indigenous microorganisms (10μL) to dilutions (1.0mL) of culture supernatants or soil extracts. The light output of indigenous microorganisms was monitored for up to 108min using a Liquid Scintillation Counter (Wallac 1410, Pharmacia).

RESULTS AND DISCUSSION

Figure 1 shows the results of the Ames test expressed as mean revertant colony counts after exposure to different co-contaminants with/without metabolic activation. The colony count values were small at diesel and lead, indicating lack of mutagenicity under these conditions due to the metabolic conversion. With chromium, the colony count values were very high because chromium showed high mutagenicity effects which may be due to the toxic effect of chromium.

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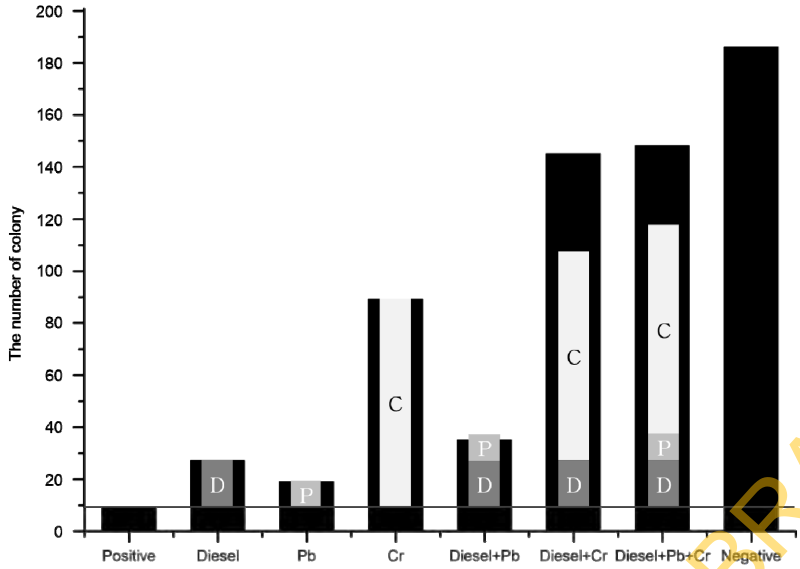

Figure 1. Mixture toxicity in organic and inorganic-combined contaminated soil by AMES test

Toxic effect in condition of co-contaminants calculated by the following equation are presented in Table 1:

Toxic effect (TE) = P(O) – P(E)

It means antagonistic, additive, and synergistic effect when the TE value is less than, near, and more than 0, respectively (Van der Geest et al., 2000). In case of Diesel + Pb, additive effect was shown because the TE value is near zero. This result indicated that there is no interaction between diesel and lead in terms of toxicity on microorganisms. However, in case of including chromium, synergistic effect was shown because TE value is above zero. The toxicity on microorganisms is increased when chromium exists with other contaminants in soil.

Table 1. Toxic effect in organic and inorganic-combined contaminated soil

	P(O)	P(E)	TOXIC effect (TE)	Effect
Diesel + Pb	0.147	0.158	-0.011	additive
Diesel + Cr	0.768	0.553	0.215	synergistic
Diesel + Pb + Cr	0.785	0.610	0.175	synergistic

CONCLUSIONS

Mixture toxicity was different according to the components of co-contaminants in the subsurface. When chromium exists with other contaminants, the soil become more toxic than individual-contaminated soil. Therefore it is important to find the factor that increases the toxicity on microorganisms when chromium existed with other contaminants in soil.

REFERENCES

Van der Geest, H. G., Greve, G. D., Blivin, M. E., Kraak, M. H. S. and van Gestel, C. A. M. (2000) Mixture toxicity of copper and diazinon to larvae of the mayfly judging additivity at different effect levels. *Environ. Toxicol. Chem.* 19(12):2900-2905

Suja, F., Pramanik, B. K. and Zain, S. M. (2009) Contamination, bioaccumulation and toxic effects of perfluorinated chemicals (PFCs) in the water environment: a review paper. *Water Sci. Technol.* 60(6):1533-1544

PILOT TEST FOR REMEDIATION OF SOIL CO-CONTAMINATED WITH PETROLEUM HYDROCARBON AND HEAVY METALS BY INTEGRATED TECHNOLOGY OF SOIL WASHING, ACTIVATED PERSULFATE OXIDATION AND NANOBUBBLE AERATION

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INTRODUCTION

Remediation of soils contaminated with petroleum hydrocarbon and heavy metals has become major environmental concerns in Korea and has complicated problems because different technologies are required for remediation of each pollutant (Dong et al., 2013). Although the co-contamination of petroleum hydrocarbon and heavy metals has been reported worldwide, little research has been performed in Korea. A pilot scale integrated process consisting of magnetic separation, activated persulfate oxidation, nanobubble aeration and soil washing with citric acid was designed and operated to remove petroleum hydrocarbon and heavy metals simultaneously or sequentially. The optimum operating conditions such as the chemical dose, reaction time and solid/liquid ratio had been obtained from lab-scale experiments before the pilot test. The aim of this study was to obtain the optimum operating conditions for the unit processes via lab-scale test and to investigate the feasibility and efficiency of remediation of soil co-contaminated with petroleum hydrocarbon and heavy metals using the integrated pilot-scale process.

METHODS

Contaminated Soil

The contaminated soil used was obtained from a former railroad station site. The soil were homogenized and sieved with a 2 mm sieve (No. 10) and then magnetically separated using magnet with 5,000 G. The soil was mainly contaminated with Zn (1,243 mg/kg), Pb (1,269 mg/kg) and TPH (841 mg/kg). The pH of the soil was 9.6.

Lab-scale Tests

Lab-scale batch tests consisted of two main steps. The 1st step is activated persulfate oxidation for petroleum hydrocarbon removal and the 2nd one is soil washing with citric acid for heavy metal removal. 100 g of magnetically separated soil was prepared in a 500 mL of polypropylene bottle. 300 mL of activated persulfate (0 - 0.1 M persulfate + 0 - 0.01 M ferrous (Fe^{2+})) was added into the bottle and mixed on a Jar tester (Hanil, Korea) at 200 - 300 rpm for 1 hr. The oxidized soil was washed (soil washing) with 300 mL of citric acid (0.1 - 2.0 M) for 1 hr at 200 - 300 rpm.

Continuous flow process was composed of persulfate oxidation and nanobubble/soil washing reactors to verify the optimum operating parameters derived from the batch tests and to obtain the nanobubble aeration time.

Pilot-scale Feasibility Tests

The pilot-scale process with 1 m^3/hr soil loading rate was composed of magnetic separation, vibrating screen, persulfate oxidation reactor, nanobubble/citric acid soil washing reactor and others in series. Three times of sampling was done with intervals of 2-3 days. All soil and liquid samples taken was immediately moved to laboratory and TPH and heavy metals were analysed.

RESULTS AND DISCUSSION

Lab-scale Tests

From lab-scale batch tests, the optimum concentrations of activated persulfate and citric acid for soil washing were obtained to be 0.1 M and 2.0 M, respectively. The other operating

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parameters such as solid/liquid ratio and contact time were also decided to be 3/1 (w/w%) and 1 hr, respectively. The removal efficiencies of heavy metals and TPH at the optimum condition are shown in Table 1. Table 2 shows the operating result of the continuous flow system.

Table 1. The lab-scale batch experiments

Content	Cu	Zn	Pb	TPH
Magnetic separated soil (mg/kg)	154	781	739	852
0.1M persulfate oxidation (mg/kg)	154	781	739	397
Soil washing (2M citric acid) (mg/kg)	44.4	378	239	385
Removal efficiency (%)	84.6	69.6	81.1	54.3

Table 2. Summary of the lab-scale continuous flow experiments

Content	Zn	Pb	TPH
Initial	326.2	303.3	1,040
Persulfate oxidation system	203.6	180.7	808
Nanobubble + soil washing system	112.8	66.5	588
Removal efficiency (%)	65.4	78.1	43.5

Pilot-scale Feasibility Tests

Fig. 1 shows the pilot-scale integrated soil washing system. The pilot plant was operated with the parameters obtained from lab-scale tests. The TPH, Cu, Zn and Pb concentrations of the soil were 564, 393, 690 and 534 mg/kg, respectively. After activated persulfate oxidation, TPH, Cu, Zn and Pb remarkably decreased with high removal efficiencies (49.5%, 37.9%, 38.6% and 42.4% for TPH, Cu, Zn and Pb, respectively). After nanobubble-soil washing, TPH and heavy metals were further removed (73.0%, 73.1%, 74.5% and 76.9% for TPH, Cu, Zn and Pb, respectively). All TPH and heavy metal concentrations satisfied the Korean soil quality criteria.

Fig. 1. The integrated soil remediation system

CONCLUSIONS

A new integrated system including activated persulfate oxidation, nanobubble and soil washing was designed and operated to remediate petroleum hydrocarbon and heavy metal contaminated soils. In summary, this system successfully removed both heavy metals and petroleum hydrocarbon with high efficiencies.

ACKNOWDEMENT

This research is financially supported by Republic of Korea Ministry of Environment as "Green Remediation Research Center for Organic-Inorganic Combined Contamination (The GAIA Project-2012000550004)".

REFERENCES

Dong, Z.Y., Huang, W.H., Xing, D.F., Zhang, H.F. (2013) Remediation of soil contaminated with petroleum and heavy metals by the integration of electrokinetics and biostimulation, *J. Hazard. Mater.* 260: 399-408.

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PHENANTHRENE CATABOLISM IN PAH-DIESEL OIL CO-CONTAMINATED SOIL

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) often exist in mixtures with other contaminants such as metals and non–aqueous phase liquids (NAPLs) among others in the environment thereby presenting serious problems for remediation (Obuekwe and Semple, 2013). Generally, most studies on PAHs which concerns their fate, behaviour, toxicity and biodegradation have focused on single PAH compounds, with minimal attention on their behaviour when present as complex mixtures in soil. One can, therefore, argue that the fate and behaviour of PAHs in mixtures may not be accurately extrapolated from single PAH focused studies. Further, much is not known of the biodegradation of complex PAH-NAPL mixtures in soil in the presence of plants.

The aims of this study were to determine the phytotoxic effects of PAH-diesel oil mixtures on two classes of plants (Leguminous versus Non-Leguminous) and assess the effect of plant presence, growing pattern, contaminant mixture and concentration, diesel amendment on the rate and extent of mineralisation of PAH.

METHODS

Pristine soil, collected from Myerscough Agricultural College, Preston, Lancashire, PR3 0RY, UK, was air dried, sieved to 2 mm and spiked with (100 mgkg^{-1} and 300 mgkg^{-1}) PAH mixture containing phenanthrene, benzo[a]pyrene and benzo[a]anthracene using acetone and toluene (12.5 ml) as carrier solvents, and amended with diesel oil (0.1 % w/w) mixture[1]. The freshly spiked soil was thoroughly blended in a mixing bowl with the aid of stainless spoon through a procedure which ensures a final homogenous soil-contaminant mixture and is of very minimal impact to indigenous soil microorganisms, and was allowed to vent in a fume cupboard for 2 h.

Pot experiments were set up in a greenhouse (completely randomised design) with each pot containing 50 g soil at field capacity and seedlings of *Medicago sativa* (Legume) and *Sorghum bicolor* (Non-Legume) were introduced both as mono- and mixed cultures. The toxic effects of the contaminants on seedling emergence, plant heights, and root to shoot ratio (R:S) were monitored over 21 d. Also, total heterotrophs and degraders (CFU g^{-1} soil) in planted and unplanted treatments were estimated following standard aseptic plate count techniques at 0, 21 and 42 d. The ratio of degraders to total heterotrophs (RDH) was calculated. Thereafter, rate and extent of PAH mineralisation was assessed via a ^{14}C-respirometry described by Reid et al., (2001).

RESULTS AND DISCUSSION

Effects of PAH mixture concentration and diesel amendment on plant emergence (%), growth, plant biomass, and height

Seedlings of *S. bicolor* (Sb) and *M. sativa* (Ms) were observed to be viable in all treatment categories as they showed 100% and 87.5% emergence respectively. However % emergence, growth, height and survival after 21 d was statistically similar (P > 0.005) to the controls which reflects the ability of both plants to tolerate PAH-diesel oil co-contaminated

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[1] In this study, soil amendments with 100 mgkg^{-1} and 300 mgkg^{-1} PAH mixture and diesel oil (D) is represented as 100+D and 300+D respectively while soil amended with only 100 mgkg^{-1} and 300 mgkg^{-1} PAH mixture without diesel oil (D) is represented as 100-D and 300-D

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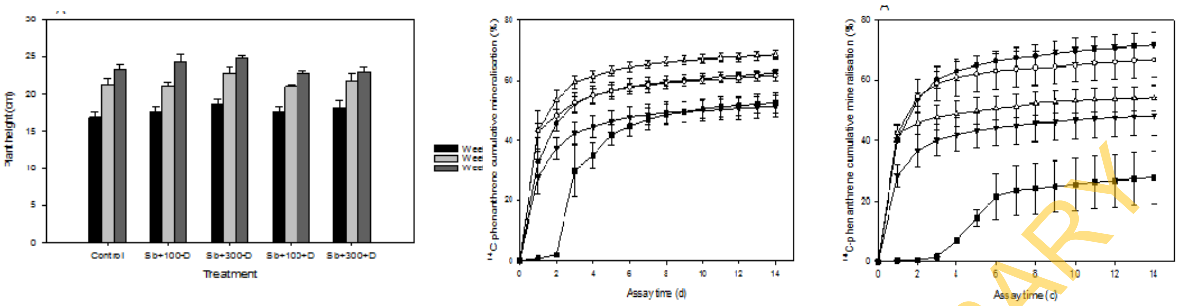
soil (Cheema et al. 2010). Hence, both plants may be potential candidates for biodegradation. Root biomass and R:S of *S. bicolor* was greater in amended soil than in clean soil unlike in *M. sativa* where the root biomass and R:S was better enhanced in clean soil (Cheema et al. 2010). Hence, *S. bicolor* is suggested to better withstand PAH-diesel oil contaminated soil than *M. sativa*.



A B C

Fig. 1. Weekly plant heights (A), and maximum extent of mineralisation in treatments associated with *S. bicolor* monocultures (B) and unplanted control (C) at 21 d.

^{14}C-phenanthrene mineralisation in soil amended with PAH-diesel oil mixture

Generally, the rates of mineralisation were statistically similar. The increase in PAH concentration resulted in an increased toxicity to indigenous microorganisms and decreased chemical availability at the onset of mineralisation, thereby, resulting in decreased rates and extents of mineralisation. However, with increasing time, rates and extents of mineralisation increased within the diesel amended soil following increased microbial adaptation, growth, and activity. In the diesel unamended treatment, only maximum rates and initial extents of mineralisation were increased. Ageing decreased the bioavailability of the ^{14}C-phenanthrene with increasing time, thereby, resulting in decreased rates and extents of mineralisation.

The monocultures of both plant species enhanced degrader numbers and associated activity in most treatments, resulting in increased rates and extents of ^{14}C-mineralisation. As a point of note, only the unplanted 100 mg kg^{-1} treatment without diesel surprisingly exhibited greater rates and extents of mineralisation than any of the planted treatment which was reflected by higher degrader numbers. Generally, the monocultures enhanced rates and extents of mineralisation than mixed cultures which may have resulted from allelopathic interaction between both species. Hence, mixed culture of both species may not guarantee an enhanced biodegradation of PAH-diesel oil contaminated soil.

Finally, the rate and extent of mineralisation was better enhanced by *S. bicolor* and *M. sativa* in the diesel unamended and amended soil respectively.

CONCLUSIONS

Sorghum bicolor and *Medicago sativa* are PAH-diesel oil mixture tolerant. However, *S. bicolor* monoculture is suggested for biodegradation purposes. Increase in PAH mixture concentration, diesel amendment, ageing, plant species and growing pattern influence rates and extents of PAH mineralisation.

REFERENCES

Cheema, S., Khan, M., Shen, C., Tang, X., Farooq, M., Chen, L., Zhang, C. and Chen, Y. (2010) Degradation of phenanthrene and pyrene in spiked soils by single and combined plants cultivation. Journal of Hazardous Materials. 177(1-3):384-389.

Obuekwe, I., and Semple, K., (2013) Impact of Zn, Cu, Al and Fe on the partitioning and bioaccessibility of C-14-phenanthrene in soil. Environmental Pollution. 180:180-189.

Reid, B., MacLeod, C., Lee, P., Morriss, A., Stokes, J. and Semple, K. (2001) A simple C-14-respirometric method for assessing microbial catabolic potential and contaminant bioavailability. Fems Microbiology Letters. 196(2):141-146.

THE EFFECTS OF CRUDE OIL CONTAMINATION ON MICROBIAL DIVERSITY IN FRESH WATER SEDIMENTS BASED ON PYROSEQUENCING STUDIES

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INTRODUCTION

Crude oils consist mainly (80–90%) of aliphatic and aromatic compounds and partly of more complex compounds such as resins and asphaltenes. Environmental contamination by crude oil therefore, poses a serious risk to the inhabitants of that environment, especially microorganisms, due to the toxicity of some of its constituents. The environmental contamination due to crude oil increases the ratio of carbon to nitrogen and phosphorus (C:N:P ratio), which has an optimum for microbial growth of 100:10:1, and the resulting nutrient imbalance is not favourable for the growth of microorganisms. Furthermore, some constituents of crude oil and/or their breakdown products, especially monocyclyic and polycyclic aromatic hydrocarbons are toxic for cells probably as a result of damage to the cell membranes and mutagenic effects on DNA. Therefore, US EPA (US Environmental Protection Agency) has included these components as priority contaminants of natural resource. In this study a pyrosequencing approach was applied to quantify the microbial diversity in fresh water sediments and the effects of crude oil contamination on the microbial community.

METHODS

Following collection of the muddy sediment samples from a local lake, in Mawson lakes-South Australia, the samples were sieved to remove debris and macroscopic plants and animals. Twenty grams of the enriched sediments placed in sterile glass tubes (50 ml vol) were spiked with different concentrations (0% as control, 1%, 2.5% and 5%) of crude oil. The tubes were incubated in a constant temperature room (25 ^{o}C) under diffused light for 10 days. After the incubation period, samples of the sediments in each tube and were blended completely, and 5 grams of these homogenous sediments were then used for DNA extraction, PCR amplification and Pro-sequencing procedure. The data obtained from GS-FLX platform sequencing submitted in Metagenome Rapid Annotation using Subsystem Technology (MG-RAST) and were analysed using the Ribosomal Data Project II (RDP II) annotation source and with regards to minimum percentage identity cut off of 97%, E-value cutoff of 1e^{-5} and minimum alignment length cutoff of 50 bp.

RESULTS AND DISCUSSION

(a) This study shows that crude oil can impact on both the microbial diversity and their relative abundances in fresh water sediment.
(b) Flavobacteriales order, and Bacterioidales (all belong to Gram negative anaerobic bacteria), Glomerellales, Rhodobacterales, Rhizobiales, Cytophagales, Gemmatimonadales, Burkholderiales and Pseudomonadales (all belong to aerobic Gram negative bacteria), Actinomycetales, Clostridiales, Bacillales, Erysipelotrichales and Lactobacillales (all belong to Gram positive bacteria) were the most dominant microorganisms in the contaminated sites.

(c) Overall, these changes in the microbial biodiversity were associated with decreases in the ratios of chemoheterotrophic microorganisms, especially aerobic bacteria, at higher levels (5%) of the crude oil contamination.

EVALUATION OF VOLATILIZATION AND BIOREMEDIATION FROM AN EXPERIMENTAL LANDFARMING ON PETROLEUM-CONTAMINATED SOILS

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INTRODUCTION

Landfarming is a biological remediation scheme that promotes aerobic biodegradation of organic contaminants in soil. Enhanced bioremediation of contaminated soil typically involves the addition of nutrients and water, and periodic tilling to mix and aerate the soil. It is popular due to its simplicity, low costs, and so on. However, there exist some inherent risks involved with landfarming, including volatilization and movement to surrounding soils/groundwater. During the process of landfarming, the total petroleum hydrocarbons (TPH), may be lost through volatilization or biodegradation (Paudyn et al., 2008). But many studies of landfarming were focus on biodegradation by microorganism and factors that affected biodegradation(Harmsen, 1991, Hoeks et al., 1988, Verstraete et al., 1976, Vanloocke et al., 1979). But the tilling process used in landfarming usually results in volatilization of lighter fractions of petroleum, while heavier fractions are degraded by biological processes(Atagana, 2003). In this study, We experimentally studied biodegradation rates and volatilization of total petroleum hydrocarbon (TPH) in an experimental landfaming pilot of acrylic reactors.

METHODS

Laboratory reactor system

The 8 reactors was made with acrylic and size was 250mm * 250mm * 250mm. Uncontaminated soils were artificially contaminated using diesel and was put into the reactors. 4 of reactors are filled with sterilized soils and other reactors consisted of soils with indigenous microorganism. The variables were Water content was 15%, 20%, 25%, 30% and no nutrients were added, but the pilot was tilled twice a week.

Reactor Sampling

Five soil samples(20-30 g) were collected for each reactors. The soil was placed in a glass vial and sealed with Teflon wrap and placed in a refrigerator until analysis. Soils were sampled every 10 days and total duration was 60 days.

Analysis of TPH in soil

A wet sample(25 g) was mixed with sodium sulphate and contaminants in soil samples were extracted using dichloromethane. Total TPH analysis for the reactor samples were analysed using gas chromatography(GC). TPH was quantified by comparing the total chromatogram peak area of the sample with that of TPH standards in dichloromethane.

RESULTS AND DISCUSSION

(a) Volatilization in sterilized soil

Figure. 1 illustrates the concentration of TPH in sterilized soil. This results indicate that volatilization of TPH increases as time goes by. Volatilization of TPH for the four moisture content of 15%, 20%, 25% and 30% was 71%, 65%, 64% and 58% in total TPH. Volatilization decreased as moisture content increased.

(b) Volatilization and biodegradation in control soil

Figure. 2 shows the concentration of TPH in soil with microorganism. This figure indicate that TPH was removed from the soil by both volatilization and bioremediation. Reduction of TPH for the four moisture content of 15%, 20%, 25% and 30% was 78%, 76%, 79%

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and 72% in total TPH. In moisture content 25%, removal efficiency of TPH is highest than others.

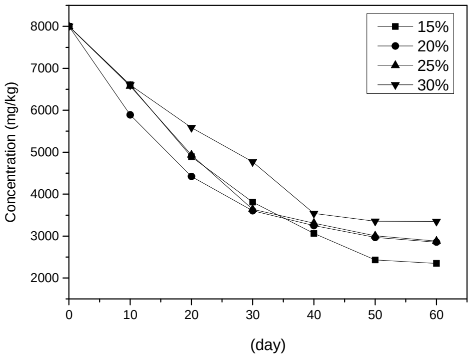

Figure 1 Concentration of TPH in sterilized soil

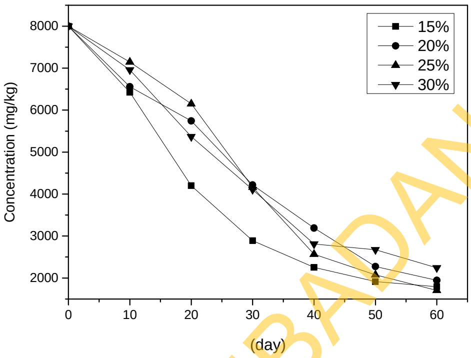

Figure. 2 Concentration of TPH in soil with microorganism

CONCLUSIONS

Laboratory experiment was performed under controlled conditions(moisture content, tilling work). In this study, average of volatilization in sterilized soil was 64% in 60 days. 76% of TPH was removed in control soil with indigenous microorganism. In control soil, removal was due to both volatilization and bioremediation. This study indicate approximate relative contribution of volatilization and bioremediation in Landfarming with moisture content and suggest Proper moisture content that decrease volatilization and help microorganism activity.

REFERENCES

ATAGANA, H. I. 2003. Bioremediation of creosote-contaminated soil: a pilot-scale landfarming evaluation. *World Journal of Microbiology and Biotechnology,* 19**,** 571-581.

HARMSEN, J. 1991. Possibilities and limitations of landfarming for cleaning contaminated soils. *on site Bioreclamation***,** 255-272.

HOEKS, J., HARMSEN, J. & PENNINGS, M. 1988. Biologische reiniging van grond vervuild met gasolie en ruwe olie volgens de landfarming-methode. ICW.

PAUDYN, K., RUTTER, A., ROWE, R. K. & POLAND, J. S. 2008. Remediation of hydrocarbon contaminated soils in the Canadian Arctic by landfarming. *Cold Regions Science and Technology,* 53**,** 102-114.

VANLOOCKE, R., VERLINDE, A. M., VERSTRAETE, W. & DE BORGER, R. 1979. Microbial release of oil from soil columns. *Environmental Science & Technology,* 13**,** 346-348.

VERSTRAETE, W., VANLOOCKE, R., DEBORGER, R. & VERLINDE, A. Modelling of the breakdown and the mobilization of hydrocarbons in unsaturated soil layers. Proceedings of the 3rd International Biodegradation Symposium. Applied Science Publishers Ltd, London, 1976. 99-112.

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CHALLENGES IN REAL FIELD IMPLEMENTATION OF RISK BASED LAND MANAGEMENT APPROACH — A CASE STUDY INVOLVING WEATHERED HYDROCARBONS

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INTRODUCTION

Risk-based land management (RBLM) is increasingly being adopted by regulators as a means of managing contaminated sites. RBLM works on the underlying basis of demonstrating no or negligible risk from exposure to contaminants to both humans and environmental receptors (Naidu et al., 2008). RBLM involves diverse approaches including an assessment of the concentration and nature of contamination, potential risk that these contaminants pose to environmental and human health, the planned use of the soil and the impact on surrounding ecosystems.

RBLM, in particular, can be applied in setting an overall sustainable development strategy for management of contaminated land in a particular region (Naidu et al., 2008; Kwame 2006). However, there are limited field based studies demonstrating the application of RBLM to management of long-term hydrocarbon contaminated soils. The objective of this study was to develop the underlying scientific basis for the risk based assessment of long-term TPH contaminated sites. In particular, the study focuses on an evaluation of the residual toxicity of stockpiled long-term hydrocarbon contaminated soils using a combination of chemical and bioassays. Along with this an assessment of the potential release of TPHs from the stockpile soils by using column leaching studies is also considered. Data gathered as part of this study was then used to formulate a strategy for the risk based management of the contaminated soils. Around 10,000 tonnes of weathered hydrocarbon contaminated soils were stockpile at an industrial site in Newman, WA. Analysis of composite stockpile samples indicated that the total petroleum hydrocarbon (TPH) concentrations in the stockpile soils are lower than the locally applicable Soil Ecological Investigation Levels (EILs) but did not achieve the target TPH concentrations stated in the remediation licence. The TPH residual fraction comprises mainly the C29 - C36 fractions and the presence of these fractions limits further bioremediation of the stockpile soils.

MULTI-SPECIES ECOLOGICAL RISK ASSESSMENT

Assay	Assessment	End point		Reference
		Acute	Chronic	
Earthworm	Survival	100% mortality	>20% mortality	OECD, Method 207(1984)
	Weight loss	100% mortality	>20% weight loss vs Control	
	Reproduction	Absence of cocoon production	Infertile cocoons, poor cocoon developments	

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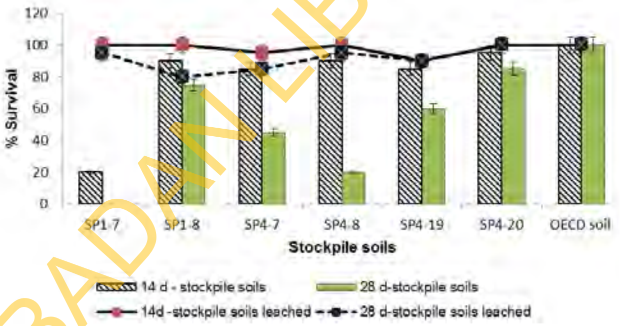
Phytotoxicity	Germination	100% mortality	>20% mortality	OECD, Method, 208 (2004)
	Growth inhibition	100% mortality	>20% difference in plant physiological parameters Vs Control	
Microbial toxicity	Changes in enzyme activity	Enzyme activity below the control soil	Enzyme activity below the control soil	Modified OECD method 217(2000)
Daphnia carinata toxicity in soil leachates	Immobilization	48h EC50 vs control >10% immobile	14 days reproduction test vs control	OECD Method 202 (1984) Liu et al. (2009)

RESULTS

Total TPH concentrations in the fifty soils analysed ranged from <100 - 1,000 mg kg^{-1}, with a median TPH concentration of 350 mg kg^{-1}. The highly volatile fractions such as the C6-C9 and C10-14 were less than the analytically quantifiable limit (10 and 50 ng ul^{-1} respectively) indicating that these TPH fractions were removed during the land-farming treatment. The C15 - C36 hydrocarbon fractions were the predominant TPH fractions present in the stockpile soils and among these, the C15 - C28 fraction ranged from <100 to 420 mg kg^{-1}.



Bioassays are general indicators of the presence of stressors in the environment. They can be divided into acute or chronic tests by looking at the selected endpoints (Hansen et al 2007). Plant germination was 100 % in all soils but post germination, seedlings except Ryegrass failed to establish. Earthworm toxicity studies found that there was a negative impact on earthworm reproduction and mortality. Further investigation of the poor plant growth and earthworm mortality revealed that it was due to the elevated salinity that developed due to surface evaporation of the saturated calcium sulphate and not residual soil TPHs. Toxicity assessment of the soil leachate on the aquatic environment showed no effect on the survival of water-flea even though the TPH concentrations in the first year leachate were as high as 1.6 mg TPH L^{-1}.

CONCLUSIONS

The field level implementation of risk based land management is not a straight forward lab to field method and requires careful consideration in case by case scenario. Our case study using the real contaminated soil revealed the challenges due to the interfering soil chemical properties which can lead to over estimation of toxicity. The results of different standard toxicity test employed in this study can be translated into risk based land management decisions. This case study suggests that caution must be exercised when using ecotoxicity tests for risk-based management of contaminated soils.

REFERENCES

Naidu R, Pollard SJT, Bolan NS, Owens G, Pruszinski AW (2008) Bioavailability: the underlying basis for risk based land management. In: Naidu et al (eds) Chemical bioavailability in terrestrial environment. Elsevier, Amsterdam, pp 53–72

Han M. Ji G. and Ni J. (2009) Washing of field weathered crude oil contaminated soil with an environmentally compatible surfactant, alkyl polyglucoside Chemosphere 76:579-586.

ANAEROBIC BIODEGRADATION OF DIESEL COMPOUNDS IN A CO-CONTAMINATED SOIL

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INTRODUCTION

Biodegradation of organic contaminants in soils has been conducted mainly in a single contaminant environment (Lee, et al. 2010). However, it may be quite different in organic-inorganic co-contaminated sites (Rocchetti, et al., 2011). In this study, the main effects of heavy metals on anaerobic biodegradation of TPH-diesel compounds was experimentally studied. The microbes which were indigenous to a site contaminated with heavy metals, such as Pb, Cr, Cu, and organic contaminants such as benzene, toluene, ethylbenzene, and xylene (BTEX) and total petroleum hydrocarbon (TPH) were applied for investigating the effects of natural attenuation in co-contaminated soil site and we also characterized adaptability of the indigenous microbes in respect to toxicities of heavy metals in batch experiments.

METHODS

Sampling and Analysis

The soil samples were from an organic-inorganic contaminated site in Korea. The samples were collected separately from the depth of 1 to 2 m and of 2 to 3 m and they were stored at 4°C in dark condition. The indigenous microorganisms were taken from soil samples and the microorganisms were cultivated and analysed with 16rRNA Sequencing. The concentration of TPH were analysed using a gas chromatograph (GC) equipped with DB-1 column (0.25 mm*30 m, 0.25 μm) and flame ionization detector (FID).

Experimental Procedures

TPH-diesel contaminated-soil samples (5 g) was incubated in 125-mL amber serum bottles with 50mL of NB medium and additional heavy metals. The head space of each bottle was purged with N_2 and capped with Teflon-silicon septa and aluminium crimp cap to maintain the anaerobic condition. Mercuric chloride ($HgCl_2$) was added to amber serum bottles for control. They were incubated in incubator at 25°C and 150 rpm. To investigate the biodegradation of diesel compounds, the serum bottles were opened after specific periods for analysis of TPH concentrations and microorganism growth changes.

RESULTS AND DISCUSSION

Figure. 1 shows the diesel degradation monitored using gas chromatography after 1, 3, 7, 14, 21, 35 days in each conditions (Diesel+Pb (DP), Diesel+Cr(DC), Diesel+Pb+Cr(DPC)). In anaerobic condition, 37-53% was degraded within 35 days. The order of TPH-diesel biodegradation was DP1>DP2>DP3>DC1>DPC1>DC2>DPC2>DC3>DPC3. This result indicates that the type and concentration of heavy metal are the most important factor for biodegrading of TPH-diesel. Especially, biodegradation efficiency significantly decreased in the presence of chromium. That is, microorganism activity for decomposing TPH-diesel was inhibited because the chromium is toxic to microorganisms.

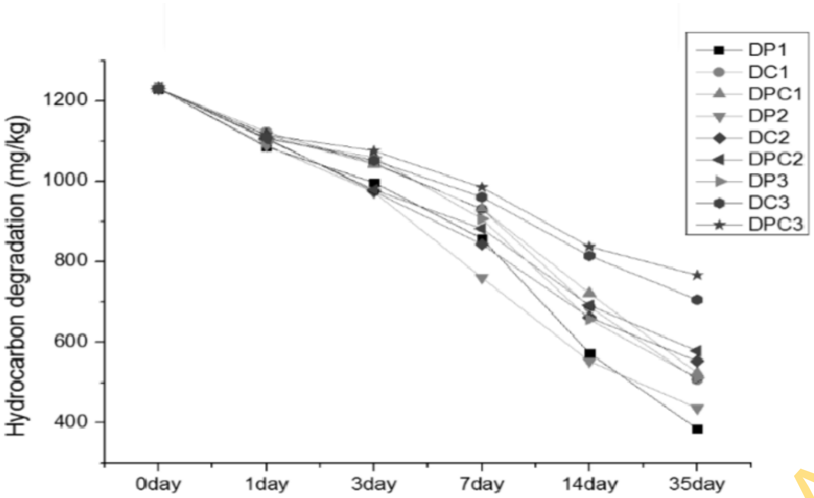

Figure 1. Concentration of TPH monitored using gas chromatography after 1, 3, 7, 14, 21, 35 days (1: low concentration, 2: medium concentration 3: high concentration).

CONCLUSIONS

TPH biodegradation efficiency was relative with type and concentration of heavy metals for biodegrading of TPH-diesel. Activities of microorganism for biodegradation were lower in condition of high concentration heavy metals than low concentration. In case of chromium, activities of microorganism is very lower than the other cases because chromium is more toxic to microorganisms than the other heavy metals.

REFERENCES

Rocchetti, L., Beolchini F., Ciani M., Dell'Anno A. (2011) Improvement of bioremediation performance for the degradation of petroleum hydrocarbons in contaminated sediments. *Applied and Environmental Soil Science*.

Y.C Lee, H.J Shin, Y.H Ahn, M.C Shin, M.J Lee, J.W Yang. (2010) Biodegradation of diesel by mixed bacteria immobilized onto a hybrid support of peat moss and additives: A batch experiment. *Journal of Hazardous Materials* 183:940–944

VALIDATION OF REMSCAN FOR THE RAPID MEASUREMENT OF PETROLEUM HYDROCARBONS IN SOIL

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INTRODUCTION

Battelle was engaged by Ziltek to test the performance of the handheld RemScan technology for the rapid measurement of total petroleum hydrocarbons (TPH) in soil (Forrester *et al*, 2013). The study was conducted in line with the former Environmental Technology Verification (ETV) program that was designed "to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about purchasing and applying these technologies". Ziltek made a number of claims relating to accuracy (<12% RSD), repeatability (<7% RSD) and detection limit (<250 mg/kg) which were also assessed as part of this study.

METHODS

Soil samples (100) were collected at each of two US Department of Defense sites; Site 1 was located at the Marine Corp Air Ground Combat Center, 29 Palms, CA and the location of Site 2 remains confidential.

For each site, 60 samples were used to build a site-specific calibration model in the RemScan instrument which was then used to scan the other 40 'blind' samples and predict their TPH concentrations; scanning was undertaken by Ziltek and then repeated by Battelle.

The RemScan predictions were compared to laboratory assay data (US EPA Method 8100 TPH) for each of the samples to determine the accuracy of the technology. Repeatability measurements were also carried out on selected samples. After two hours of formal training, Battelle staff were asked to comment on a number of usability claims and to fill out a usability questionnaire.

RESULTS AND DISCUSSION

For Site 1, the accuracy of RemScan was 9.4% RSD compared to accredited laboratory data, and the repeatability was 1.8% RSD. For Site 2, the accuracy could not be calculated due to lack of data points between 5,000 and 10,000 mg/kg and the repeatability was 3.3% (when adjusted for volatilization effects). The detection limit of the method for both sites was around 65 mg/kg (at 1 st. dev.) which compares very favourably with commercial laboratories.

Using a regulatory criteria of 1,000 mg/kg, there were no false negatives or positives for either test site, which means that the RemScan technology could have been used confidently at these sites with no requirements for laboratory analysis.

The main limitation of the RemScan technology is the requirement for soil moisture to be less than 8% for accurate readings. The latest release of RemScan notifies the user when moisture in the sample is too high to obtain accurate results. High carbonate caused an under-prediction of TPH for three samples from Site 1, however in a normal commercial setting this would be overcome by including a wider range of carbonate samples in the calibration model.

CONCLUSIONS

All Vendor Claims relating to accuracy (<12% RSD), repeatability (<7% RSD), and detection limit (<250 mg/kg) were independently verified by Battelle during the blind study. Two Battelle staff rated RemScan extremely easy to use with minimal training (10/10).

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REFERENCES

Forrester ST, Janik LJ, McLaughlin MJ, Soriano-Disla JM, Stewart R, Dearman B (2013) Total petroleum hydrocarbon concentration prediction in soils using diffuse reflectance infrared spectroscopy. *Soil Science Society of America Journal* 77(2), 450-460.

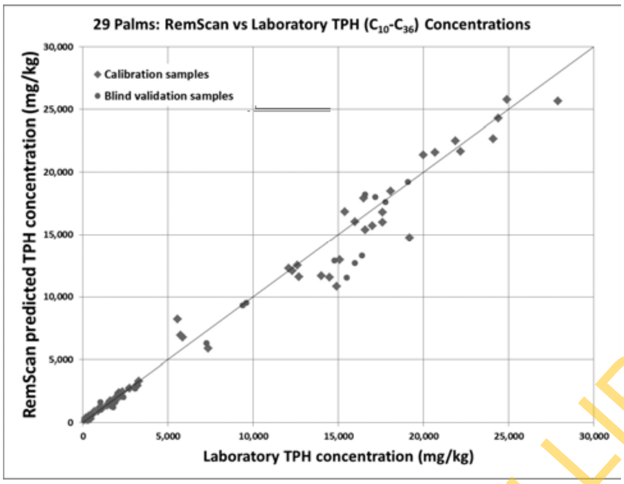

Fig. 1. RemScan predictions versus laboratory assay values for calibration samples and blind validation samples for the 29 Palms test site

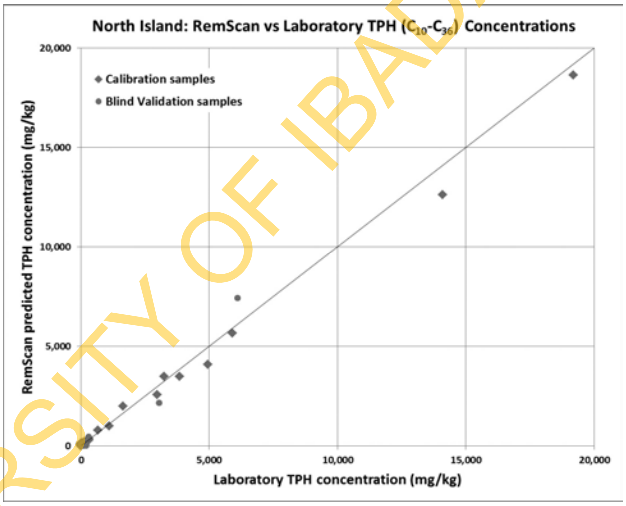

Fig. 2. RemScan predictions versus laboratory values for calibration samples and blind validation samples for Site 2.

Table 1. Summary of RemScan Performance

	Site 1	Site 2	Vendor Claims Met
Accuracy	9.4%	N/A	Yes
Repeatability	1.8%	3.3%	Yes
Detection limit	66 mg/kg	64 mg/kg	Yes
False positives/ negatives (1,000 mg/kg)	Nil	Nil	N/A
Battery life	Full day of continuous use with one battery swap		
Throughput rate	10-20 samples per hour		
Operational cost	No incremental cost		
Breakeven cost threshold	7 days (1,400 samples)		
Formal training required	<2 hours		
Infield calibration time	3 minutes every hour		

P40

MULTIPHASE MODELLING OF LNAPL REMEDIATION OPTIONS IN AQUIFERS WITH COMPLEX GEOLOGIES

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INTRODUCTION

Uncertainties arising from dealing with LNAPL contamination in complex environments have strong technical, environmental, economic and regulatory compliance implications. Following a modelling approach, this research focuses on two correlated questions. First, how geological parametric uncertainty affects the estimation of remediation endpoints as well as other critical elements of characterisation, risk reduction and remediation performance. Second, how this information can be used to guide field work aimed at site and contaminant characterisation, for instance by assessing which features and parameters are most important and what level of detail might be required in their assessment.

OBJECTIVES

The main research objectives are to:

- (a) Develop mathematical models calibrated and validated against field observations
- (b) Determine remediation endpoints for different technologies, sites and scenarios
- (c) Determine the influence of site geology and LNAPL composition on LNAPL behaviour and remediation performance and thereby guide site characterisation
- (d) Assess the level of complexity required by the models to provide defensibly results with a view to testing and improving simpler tools for predicting endpoints

RESEARCH FRAMEWORK

Data collection methods such as pumping and tracer tests, detailed core analyses, borehole geophysics and sampling in multilevel wells are being applied to determining the spatial variability of key parameters and also identify overprinting structures in two selected sites, a fine-textured aquifer in Western Australia and a fractured crystalline rock aquifer in Victoria.
Validated multicomponent multiphase models can be used to run predictive simulations and provide estimations of remediation endpoints for different technologies and site conditions.
The influence of parameters such as the scale, magnitude and correlation of variability as well as structural connectivity and matrix diffusion are being assessed through application of different conceptual site models, sensitivity analyses and uncertainty quantification methods.
Coupled with field observations, scenario modelling is giving information about the controlling processes and the range of parameters that may be encountered. In the first instance, a scenario which maintains the basic three layer conceptual site model for the fine-textured aquifer site was built. The effects of defining more layers where hydraulic conductivities were assigned as either constant values or random fields for the simulation of LNAPL recovery were quantified.

CONCLUSIONS

Mathematical modelling allows an extension to the range of settings and conditions for which remediation performance can be tested, as well as the constrained temporal range of field remediation trials. In this way, this research has helped to improve the underlying knowledge and conceptual site models allowing more informed decisions on the assessment and management of LNAPL contamination in such complex geologies. It was shown that spatial variability of the hydraulic conductivity field strongly determines the LNAPL distribution and hence the remediation performance as well as the variability of LNAPL recovery.

USING HYDRAULIC TESTING TO EVALUATE LNAPL RECOVERY IN FINE GRAINED SYSTEMS

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INTRODUCTION

Petroleum fuels are the most common and widespread contaminants requiring management in urban and industrial environments. These contaminants are commonly referred to as light non-aqueous phase liquids (LNAPLs)(Johnston 2010). LNAPLs are hydrophobic liquid organic chemicals with lower density than water and immiscible with water. They include a wide range of substances, but the most common types are oils and fuels, such as diesel, jet fuel and petrol (gasoline) (Kirkman, Adamski & Hawthorne 2013).

In the present study the recovery of LNAPLs from a gasoline fine grained contaminated site in Western Australia is measured. The aim of this work is to evaluate the LNAPL recovery of the site via short term baildown tests versus recovery trials. Baildown tests have been proposed as a metric for the estimation of NAPL recovery but the majority have been conducted in homogeneous settings with little existed data from more complex subsurfaces. The calculation of the LNAPL transmissivity values was the outcome of the recovery tests. Wells with similar transmissivity values can be used and compared easier later during the remediation processes.

METHODS

The short term baildown recovery tests took place via bailers according to ASTM standards (ASTM 2013) in two different time periods. The recovery took place via skimming trials. Five wells with product were used to conduct the transmissivity tests. The estimation of LNAPL transmissivity of the site was approached by the Bowers & Rice and Copper & Jacob methods (Jacob & Lohman 1952) (Bouwer & Rice 1976) (Chaberneau, Kirkman & Muthu 2012). Finally, for the measurement of ground water and NAPL levels an oil/water interface probe was used.

RESULTS AND DISCUSSION

The first time period of baildown tests was between 24/6 and 24/9 of 2014. The second period for the baildown tests will be between 5/5/2015- 8/5/2015. In this time period the water table elevation is lower compared to the first tested period and the recovery of LNAPLs is anticipated to be higher. The recovery trials will take place at the end of May.

CONCLUSIONS

The LNAPL recovery of a fine grained site was estimated by baildown testing in two different time periods of different water table elevations. The results were compared with recovery trials. The aim of this research is to evaluate how precise could be a prediction of the LNAPL recovery of a site using short term baildown tests.

REFERENCES

ASTM 2013, *The standard Guide for Estmation of LNAPL Transmissivity ASTM E2856-13*.

Bouwer, H. & Rice, R.C. 1976, 'A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells', *Water Resources Research*, vol. 12, no. 3, pp. 423-8.

Chaberneau, R.J., Kirkman, A.J. & Muthu, R. 2012, *API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis*.

Jacob, C.E. & Lohman, S.W. 1952, 'Nonsteady flow to a well of constant drawdown in an extensive aquifer', *Eos, Transactions American Geophysical Union*, vol. 33, no. 4, pp. 559-69.

Johnston, C.D. 2010, '*CRC CARE Tech. Report 18*- Selecting and assessing strategies for remediating LNAPL in soils and aquifers'.

Kirkman, A.J., Adamski, M. & Hawthorne, J.M. 2013, 'Identification and Assessment of Confined and Perched LNAPL Conditions', *Groundwater Monitoring & Remediation*, vol. 33, no. 1, pp. 75-86.

SOIL VAPOUR PASSIVE SAMPLING: STARVATION EFFECT TESTING AND VERIFICATION

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INTRODUCTION

The collection and interpretation of soil vapour data is becoming an increasingly important phase of site characterisation in relation to health risk assessments and site remediation. Various methods and sample media can be used to assess soil vapour concentrations, all of which can be described as either *passive* or *active*, in nature. While the latter are generally considered to provide 'definitive' soil vapour concentration data, they usually require a permanent sub-surface installation and specialist, calibrated sampling equipment and training. Data obtained from passive sampling is often considered to be of a *first-pass screening* level, however, the simplicity of the installation and the potential cost saving over active sampling can permit increased deployment providing a further reaching and/or a denser spatial network of soil vapour data to be generated. This can lead to a much greater understanding of potential sources and the distribution of soil vapour impacts and hence evaluation of the risk profile posed by soil vapour at a site.

A potential limitation of passive sampling in soils is the 'starvation effect', where the known diffusive uptake rate of vapours through the membrane containing the sample media is greater than the diffusive rate of vapours through the surrounding soil. This can 'starve' the sampler of vapour, potentially leading to the under-reporting of soil vapour concentrations by an order of magnitude or more. This can be an issue in clays, such as those beneath Melbourne and much of Victoria.

Here we present the findings of a limited study to evaluate the potential effect of starvation on the results of a large scale survey by varying sampler deployment time and verifying passive results using active sampling methods. The primary objective of the passive sampling was to identify potential sources of impact on the operational site.

METHODS

A soil vapour survey was conducted at a manufacturing facility in Melbourne in 2013 deploying around 100 passive samplers (SiREM Waterloo Membrane Samplers) at 1 m bgl over an 4 ha site as part of a *clean-up* investigation. The chemicals of concern were primarily chlorinated solvents and BTEX. To study the potential starvation effect, 5 secondary samplers were co-located in separate sampling auger holes immediately adjacent to 5 of the primary samplers, but deployed for only a 24 hour period. In addition, 3 soil vapour wells were installed from which 'active' samples were collected using SUMMA canisters.

Rational

Soil vapour concentration can be calculated from the mass adsorbed onto the sample media, the sample time and the known compound diffusive rate of the membrane. By deploying samplers for different lengths of time in the same soils and comparing the mass adsorbed by each, the starvation effect, if present, can be tested.

In addition, collection and analysis of vapour samples using SUMMA canisters located <1 m from passive sampler locations may allow these sampler results to be 'calibrated'.

RESULTS AND DISCUSSION

Primary Passive Samplers

Concentrations reported for the primary passive samplers (7-day deployment) ranged from below the LOR to 1500 mg/m^3 for BTEX compounds and to 2.7 mg/m^3 for chlorinated

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solvents. Areas of impact were clearly identified by the survey (contour map generated from results) and linked to known historical information about the site or known off-site sources.

Secondary Passive Samplers

Concentrations reported for the secondary passive samplers (1-day deployment) located within <1 m from primary samplers were in general much higher than those of their counterparts due to adsorbing comparable compound masses (Table 1). This suggests that vapour adsorption occurred mainly within the first 24 hours of the deployment, the 7-day samplers being effectively starved for the remaining 6 days. This means the reported primary sampler concentrations are potentially ~14% of the actual concentration, bearing in mind that the 1-day sampler results could also have been subjected to the starvation effect.

Table 1. Example Passive sampler results: 7-day versus 1-day deployment.

	Reported Concentration			Mass	
Compound	7-Day (mg/m^3)	1-Day (mg/m^3)	1-Day / 7-Day (%)	7-Day (mg)	1-Day (mg)
Benzene	0.11	0.51	460	0.0025	0.0016
Toluene	0.34	0.070	21	0.015	0.00043
Ethyl Benzene	2.9	29	1000	0.20	0.28
m,p-Xylene	7.4	66	890	0.48	0.60
o-Xylene	1.2	0.30	25	0.084	0.0031

SUMMA Canister Verification

Where results were reported above the LOR, concentrations reported for SUMMA canister samples (collected using usual QC measures, e.g. helium shroud leak check) in general returned concentrations much greater than the corresponding primary passive sampler concentrations. In the example comparison provided in Table 2, while the variation in the ratios of the concentrations calculated by active and passive methods is relatively large, a conservative approach could be used to 'calibrate' all passive sampler results using a few representative active results.

Table 2. Example Active versus passive results:

	Reported Concentration		
Compound	Active (mg/m^3)	7-Day Passive (mg/m^3)	Active / Passive (%)
Vinyl Chloride	<0.05	<0.04	-
cis-1,2-Dichlorethene	0.51	0.029	1800
Chloroform	0.12	0.033	360
Trichloroethene	19	2.7	700
Tetrachloroethene	0.22	0.018	1200

CONCLUSIONS

Ideally, if passive samplers are to be used to verify actual soil gas concentrations, a small number of samplers should be deployed at a similar location for different time periods to test starvation effect and obtain ideal deployment time. Since the time of this work, significant additional literature is now available that demonstrates that the selection of sampler, uptake rate, sampling void size and duration of sampler deployment and site calibration are all important considerations in the design of a passive soil vapour survey. The limited data from this survey supports some of the findings from this research by indicating that, in general, shorter deployment duration in clays is likely to provide vapour concentrations that are a closer correlation to those measured in the active samples. Overall, it is considered that the current best practice for low permeability basaltic clay soils is likely to be a combination of using passive samplers to identify areas of concern and active sampling to cross correlate and hence understand the overall picture of soil vapour distribution and risk.

PROFICIENCY TESTING OF LABORATORIES MEASURING POLLUTANTS IN ENVIRONMNETAL MATRICES

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INTRODUCTION

Proficiency testing (PT) is an important quality assurance tool for testing laboratories and participation in PT is a requirement for accreditation to the ISO 17025[1] standard. The National Measurement Institute (NMI) conducts interlaboratory proficiency testing of the identification and measurement of metals, anions, pesticide and hydrocarbon pollutants in soil and water. Laboratories in Australia, Asia, and Africa have participated. In 2015 a PT for the measurement of PFOS and PFOA in water and soil was introduced. All PTs were conducted according to ISO 17043[2].

METHODS

Test samples were either taken from contaminated sites, or prepared by spiking uncontaminated soil or water with metals or organic pollutants. The homogeneity and stability of the test samples were assessed. Participant laboratories measured the pollutants using their normal test methods and returned a single result and associated measurement uncertainty for each analyte. Participant results were processed using robust statistical methods and participants' performance assessed using z-scores and E_n-scores[3].

RESULTS AND DISCUSSION

Recently completed proficiency studies are reported. Figure 1 illustrates results reported for the analysis of semi-volatile hydrocarbon pollutants in soil. Figure 2 illustrates results reported for the analysis of mercury is sludge.

Trends in areas such as analytical performance, participation and reporting of uncertainty were identified. There has been an improvement in the measurement of semi-volatile hydrocarbons in soils following the release of the new NEPM guidelines[4]. Other measurements, such as the measurement of pesticides in soil have shown no improvement. A greater acceptance and understanding of measurement uncertainty was evident.

CONCLUSIONS

Proficiency testing is useful for laboratories and decision makers to assess analytical data and identify any need for corrective action. The NMI PT program has demonstrated that results from laboratories measuring pollutants in environmental matrices are not always in agreement.

REFERENCES

ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (2005) ISO, Geneva, Switzerland.

ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing, (2010) ISO, Geneva.

ISO13528:2005(E), Statistical methods for use in proficiency testing by interlaboratory comparisons, (2005) ISO, Geneva, Switzerland.

National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013, http://www.comlaw.gov.au/Details/F2013L00768 (Accessed April 2015).

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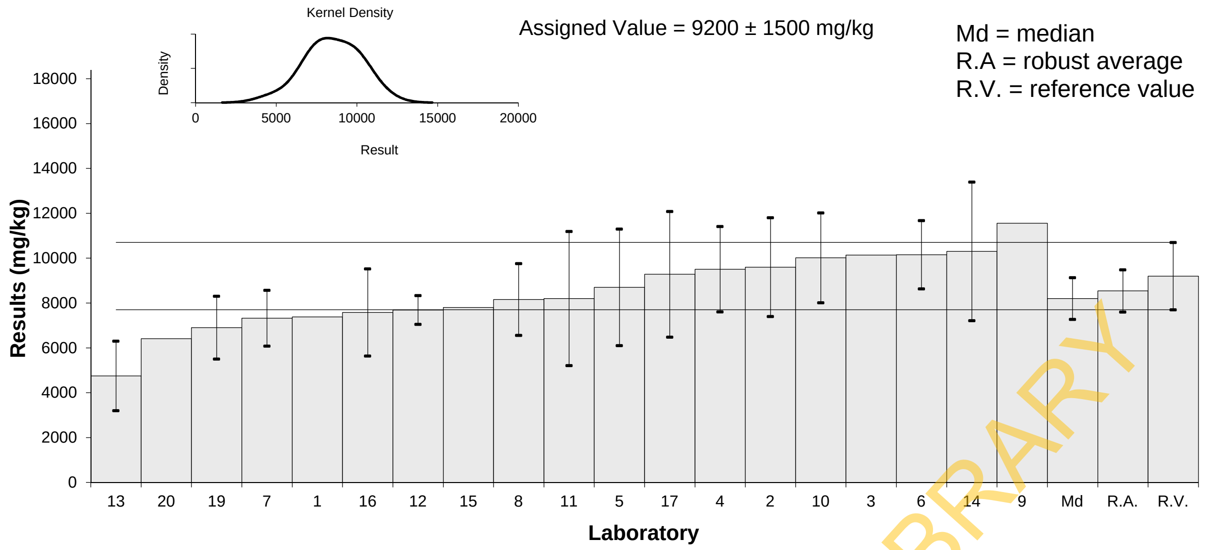

Fig. 1. Proficiency test results for semi-volatile hydrocarbon in soil

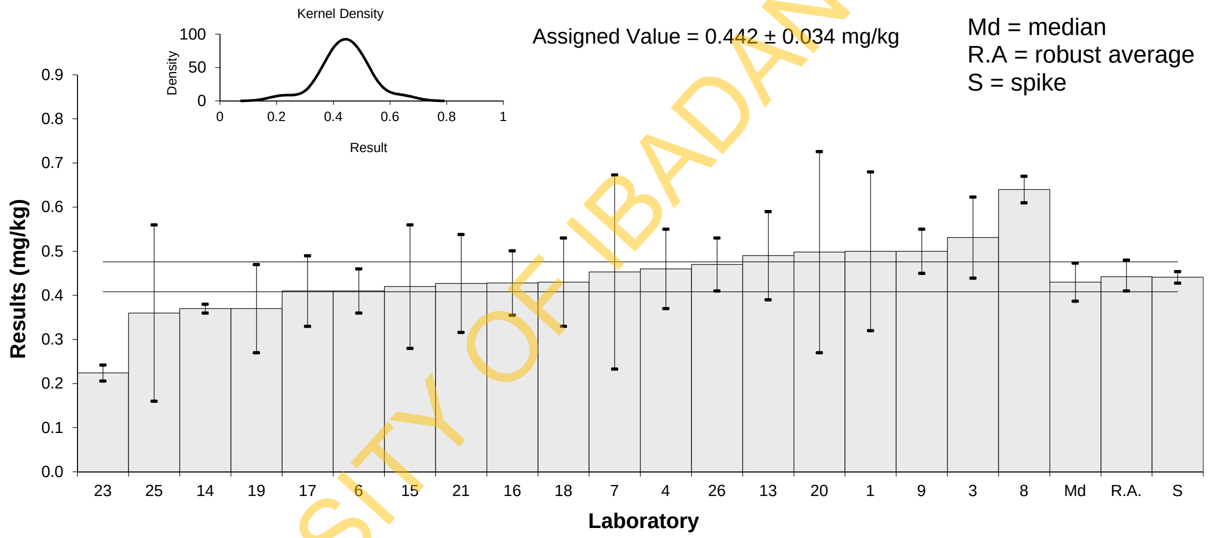

Fig. 2. Proficiency test results, mercury in sewerage sludge

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REFINED LVI-PTV-GC-MS FOR ANALYSIS OF LOW LEVEL POLYCYCLIC AROMATIC HYDROCARBONS IN CONTAMINATED GROUNDWATER AND SOIL SAMPLES

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INTRODUCTION

In environmental monitoring of polycyclic aromatic hydrocarbons (PAHs), a robust method for analysing low level contamination is required to meet regulatory limits. Current monitoring methods use large volume extraction and manual pre-concentration prior to chromatographic separation which result to analyte losses. The detection limits of conventional Gas Chromatography-Mass Spectrometry (GC-MS) methods can only allow sample injection volumes to a maximum of 5 µL. To address these issues, this study developed, optimised and validated a routinely practical method to improve detection limit of PAHs in contaminated groundwater and soil samples. The application of Large Volume Injection (LVI) by means of Programmed Temperature Vaporization (PTV) technique was investigated for the analysis of PAHs by GC-MS.

METHODS

Materials

Working standard solutions were prepared for linearity, precision and recovery determinations using n-pentane as solvent. Laboratory controls were prepared from PAHs-free soil (sandy soil pre-washed with methanol and n-pentane) and Milli Q water samples. Spiked samples were fortified by adding a known amount of standard to the laboratory control and matrix samples.

Experimental

The factors affecting the performance of the LVI-PTV technique for the GC-MS determination of PAHs were examined by comparing standard responses at different injection speed mode, injection volume, initial liner temperature, inlet pressure, vent flow and vent time.

The performance characteristics of the method were verified for the 16 PAHs listed by the United States Environment Protection Agency (USEPA) as priority pollutants. Quality parameters namely, accuracy, precision, linearity and limit of quantification were determined.

RESULTS AND DISCUSSION

The large volume extraction and manual pre-concentration steps were eliminated by extracting the analytes in situ from the environmental sample and introducing a large volume of the extract into the PTV inlet of the GC-MS. A 20 µL sample was injected at an initial temperature of 10°C, thus, reducing analyte degradation. After injection, the temperature was increased to evaporate the solvent through the split vent line with helium at a vent flow of 25.0 ml/min for 0.90 min, hence pre-concentrating the sample. The ballistic heating and cooling capability of PTV provides flexibility which is not possible with the conventional GC-MS injection modes. Optimisation of LVI-PTV procedure obtained good chromatography for the PAH peaks. Figure 1 displays the resolution of the 16-component PAH standard mixture.

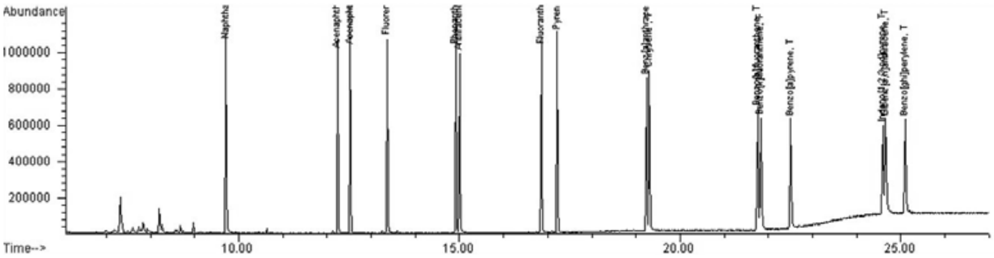

Figure 1. Total ion chromatogram of a standard PAH solution showing resolution, with retention order according to Table 1.

Validation of the method showed linear response having R^2 values of 0.998–0.999 for the concentration range of 100–8000 ppb. Recovery percentages were 95–121% (6.3% RSD) and 98–118% (4.4% RSD) for the soil laboratory control spike and matrix spike, respectively. Water samples have recovery values of 81–91% (3.1% RSD) and 84–96% (4.2% RSD) for the laboratory control spike and matrix spike, respectively. A quantification/reporting value of 4 parts per billion (ppb) was selected as the in-house limit. Six replicate injections of this concentration were performed and at this level, the method produced results within +/- 0.7 ppb at 95% confidence level, as shown in Table 1.

Table 1. Precision (n=6) of chosen in-house limit of quantification/reporting value solution

Retention Order	Analyte	Average (ppb)	Standard Deviation	2 x Standard Deviation
1	Naphthalene	3.94	0.17	0.34
2	Acenaphthylene	4.71	0.06	0.12
3	Acenaphthene	3.99	0.11	0.22
4	Fluorene	4.43	0.07	0.14
5	Phenanthrene	4.45	0.10	0.20
6	Anthracene	4.48	0.23	0.46
7	Fluoranthene	4.34	0.12	0.24
8	Pyrene	4.25	0.18	0.36
9	Benzo[a]anthracene	5.17	0.13	0.26
10	Chrysene	4.00	0.17	0.34
11	Benzo[b]fluoranthene	4.56	0.09	0.18
12	Benzo[k]fluoranthene	4.56	0.09	0.18
13	Benzo[a]pyrene	5.01	0.09	0.18
14	Indeno[1,2,3-cd]pyrene	5.77	0.11	0.22
15	Dibenz[a,h]anthracene	5.06	0.36	0.72
16	Benzo[ghi]perylene	4.43	0.09	0.18

CONCLUSION

This study successfully demonstrated the application of a LVI-PTV approach for the GC-MS analysis of low level PAHs in contaminated groundwater and soil samples. In PTV solvent vent mode, sample pre-concentration of a 20 µl injection occurs inside the inert liner in a highly controlled and automated manner; thus, enabling a limit of quantification at 4 ppb level.

REFERENCES

Cortes, J. E., A. Susses, et al. (2012) Total petroleum hydrocarbons by gas chromatography in Colombian waters and soils. *American Journal of Environmental Sciences* 8(4): 396-402.

Delgadillo-Marin, M.,Pena-Alvarez, A., Villalobos, M. (2013) Application of Programmed Temperature Vaporization Large Volume Injection Gas Chromatography (PTV-LVI-GC) to the Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils. *Journal of Mexican Chemical Society* 57(2): 85-91.

DIFFERENTIAL GENE EXPRESSION ANALYSIS IN *EISENIA FETIDA* CHRONICALLY EXPOSED TO BENZO(A)PYRENE

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INTRODUCTION

Benzo(a)pyrene (BaP) is a well-established carcinogen and mutagen that belongs to polycyclic aromatic hydrocarbons (PAHs) group of chemicals. BaP and other PAHs are derived as a result of incomplete combustion of fossil fuel and organic materials (Yunker et al., 2002). BaP reaches the environment from domestic emissions and wastes, automobile exhausts, industrial emission, agricultural activities and also by some natural sources (Ravindra et al., 2008). BaP has been found to accumulate in several organisms such as (Subashchandrabose et al., 2014), mussels (Canova et al., 1998) and mouse (Uno et al., 2006). BaP is known to be mutagenic in somatic cells.

Analysing global transcription effect in an organism might reveal potential toxic effect as well as the toxicological mechanisms (Huang et al., 2014). Since soil is the largest sink for BaP it is essential to use terrestrial organism such as the *Eisenia fetida* (earthworm), to develop molecular biomarkers by studying the differential gene expression in response to BaP. Alteration in gene expression profile would be a powerful tool to diagnose the effects of a toxic pollutant such as BaP at very low levels. Next generation mRNA sequencing is one of the tools available these days to analyse such changes in gene expression profiles. *E. fetida* was chronically exposed to 10 mg/kg of BaP for about eight months and the gene expression profile was studied.

METHODS

Eisenia fetida were maintained in natural soil supplemented with fruits and vegetable waste, at 25 ±1 °C, about 80% humidity and a 16:8 h Light: dark cycle in our laboratory. Soil was collected, air dried and sieved through 2 mm sieve. *Eisenia fetida* were exposed to BaP at concentration of 10 mg kg^{-1}; controls were maintained simultaneously. Total RNA was isolated and subjected to paired-end RNA sequencing at The Ramaciotti Centre for Gene Function Analysis using Illumina HiSeq 2000.

The forward and reverse raw RNA sequence reads were joined separately and analysed using Trinity software (Grabherr et al., 2011) installed in bigmem-1024 server, eRSA, Adelaide. Forward and reverse library were used to assemble transcripts and minimum reads to join k-mers was set at 2 and glue was set at 4. The assembled transcripts were translated and longest possible ORFs with >130 amino acids were selected and annotated using stand-alone BLAST (NCBI-BLAST-2.2.28+) using UniProt database. NPKF- normalized counts were compared and the transcripts that are more than fourfold higher expressed with the significance of $p = 0.001$ were selected for analysis.

RESULTS AND DISCUSSION

BaP alters major genes that are involved in calcium homeostasis, protein transport, cytoskeletal structure, nucleotide binding and cell cycle regulation inflammatory response, vasodilation, Cell division microtubule-based movement, Lipid metabolic process, DNA binding, spermatogenesis, embryo development ending in birth or egg hatching, establishment of protein localization, wound healing, nervous system development, and eye development in *Eisenia fetida*. This report will help understand the toxicological effects at molecular level and to develop molecular markers for BaP contaminated soil. Furthermore, the genes that are highly specific to BaP exposure can be developed into a biomarker.

CONCLUSIONS

1. Transcriptome assembly followed by differential gene expression has revealed several BaP induced genes.
2. The genes that are highly altered and specific to BaP can be developed into molecular biomarkers.

REFERENCES

CANOVA, S., DEGAN, P., PETERS, L. D., LIVINGSTONE, D. R., VOLTAN, R. & VENIER, P. 1998. Tissue dose, DNA adducts, oxidative DNA damage and CYP1A-immunopositive proteins in mussels exposed to waterborne benzo[a]pyrene. *Mutat. Res,* 399**,** 17-30.

GRABHERR, M. G., HAAS, B. J., YASSOUR, M., LEVIN, J. Z., THOMPSON, D. A., AMIT, I., ADICONIS, X., FAN, L., RAYCHOWDHURY, R., ZENG, Q., CHEN, Z., MAUCELI, E., HACOHEN, N., GNIRKE, A., RHIND, N., DI PALMA, F., BIRREN, B. W., NUSBAUM, C., LINDBLAD-TOH, K., FRIEDMAN, N. & REGEV, A. 2011. Full-length transcriptome assembly from RNA-Seq data without a reference genome. *Nat Biotechnol,* 29**,** 644-52.

HUANG, L., ZUO, Z., ZHANG, Y., WU, M., LIN, J. J. & WANG, C. 2014. Use of toxicogenomics to predict the potential toxic effect of Benzo(a)pyrene on zebrafish embryos: ocular developmental toxicity. *Chemosphere,* 108**,** 55-61.

RAVINDRA, K., SOKHI, R. & VAN GRIEKEN, R. 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment,* 42**,** 2895-2921.

SUBASHCHANDRABOSE, S. R., KRISHNAN, K., GRATTON, E., MEGHARAJ, M. & NAIDU, R. 2014. Potential of fluorescence imaging techniques to monitor mutagenic PAH uptake by microalga. *Environ Sci Technol,* 48**,** 9152-60.

UNO, S., DALTON, T. P., DRAGIN, N., CURRAN, C. P., DERKENNE, S., MILLER, M. L., SHERTZER, H. G., GONZALEZ, F. J. & NEBERT, D. W. 2006. Oral benzo[a]pyrene in Cyp1 knockout mouse lines: CYP1A1 important in detoxication, CYP1B1 metabolism required for immune damage independent of total-body burden and clearance rate. *Mol Pharmacol,* 69**,** 1103-14.

YUNKER, M. B., MACDONALD, R. W., VINGARZAN, R., MITCHELL, R. H., GOYETTE, D. & SYLVESTRE, S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry,* 33**,** 489-515.

ASSESSMENT OF CONTAMINATION FOLLOWING SIMULATED CHEMICAL AND BIOLOGICAL ATTACKS IN A PUBLIC BUILDING

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INTRODUCTION

There is currently a gap in Australia's preparedness for a large-scale chemical or biological attack on a public building or other significant infrastructure. This paper reports on a project which addresses the gap relating to the procedures of evacuation, contamination assessment and decontamination of public buildings following a terrorist release event. The research performed simulates a fictitious chemical (methyl isocyanate) and biological (Anthrax) terrorist attack on a public building of political importance in Western Australia. To characterise the spread of such contaminants and determine the effectiveness of decontamination efforts in order to declare a facility safe for public occupancy requires significant effort.

METHODS

Sulfur hexafluoride (SF6) as a simulant for methylisocyanate and Bacillus thuringiensis (Bt) formulation (Dipel®) as a simulant for Anthrax were released in a disused laboratory/office facility. The Bt spores were released from an envelope and tracked by collection on deposition plates and the SF6 by real time measurement with infrared spectrometry and by sample collection in foil bags followed by laboratory analysis by gas chromatography with electron capture detection (GC-ECD).
A Data Quality Object (DQO) document was written to capture all information pertinent to the decision making process for pre and post-decontamination phases of the study. The sampling plan was determined and the degree of contamination subsequently visualised using software tools (VSP).
Pseudo-real time monitoring of chemical and biological simulant species allowed the flux and dispersion of 'agents' to be evaluated.

RESULTS and DISCUSSION

In the initial release and resuspension experiment, nine sampling points in each room were used to construct a concentration or spore density gradient map.

Fig 1 summarises the data for the release of Bt. High spore numbers were observed in the room where the envelope was opened and in rooms where ambient air is actively drawn in to the room whereas rooms with powerful air conditioning inlets tended to have low spore numbers indicating that spores tended to travel in the direction of the prevailing air flow. Spores were observed in the most distant rooms from the release room indicating that a release of only 350 mg of bacteria (7% w/w B. thuringiencis in preparation) will result in observable spore concentrations some 40 m from release.

Both spore counts (Fig 1) and SF6 concentration (Fig 2) reached maximum values in the release room and in rooms where building air is actively drawn in, i.e. rooms which had powerful air extraction infrastructure. As SF6 was observed in rooms far removed from the release room, the implication for first responders is that personal protective equipment should be worn even if operations are not being conducted in the vicinity of the release room as exposure to toxic gas is likely, albeit at low concentrations.

Linear regression analysis revealed a correlation between spore counts and SF6 concentration ($p = 0.05$). The observation that spores will be deposited on surfaces in almost all rooms of the building will have implications for contamination assessment and decontamination. Decontamination efforts cannot be confined to the release room only and assessment of colony count/room in all rooms is prudent.

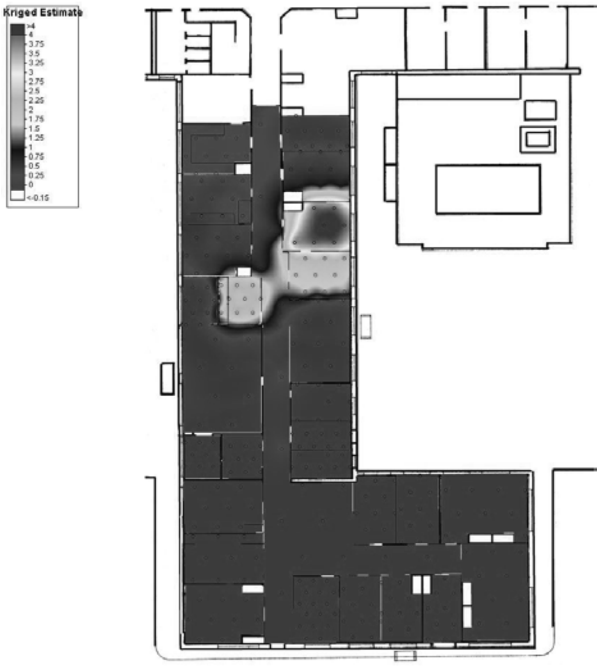

Fig 1. Geostatistical map of median colony counts room following initial release of Bt (0-120 minutes)

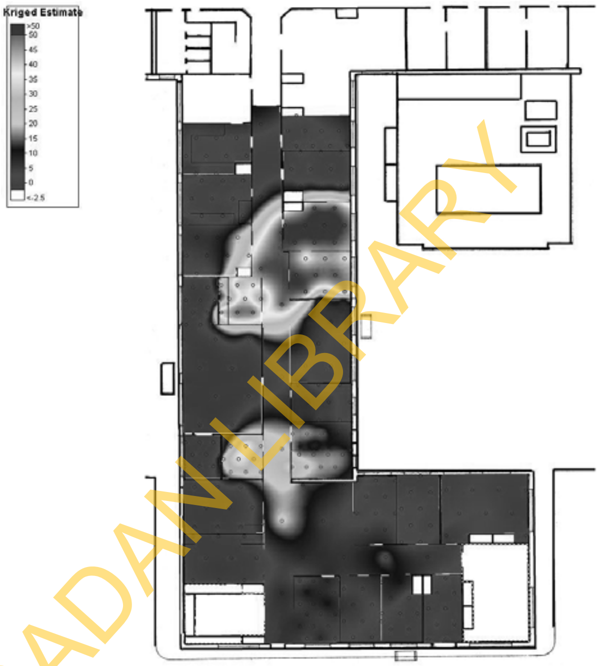

Fig 2 Maximum SF6 concentrations in each room at 3 minutes after release

CONCLUSIONS

Of interest are the findings that spores travel to the building periphery in a short timescale and that months after the building had been left unoccupied it was possible to re-suspend viable spores simply by walking through the affected area. This has implications for first responders investigating suspicious substance or “white powder” incidents. First responders are likely to be called within the timescale of the release experiment (2 hours). Therefore the implication for first responders is that personal protective equipment should be worn even if operations are not being conducted in the vicinity of the release room as exposure to spores is possible.

A FRAMEWORK FOR PRELIMINARY ASSESSMENT OF VULNERABILITY TO CONTAMINATION OF SOIL AND GROUNDWATER IN CHEMICAL ACCIDENTS

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INTRODUCTION

In South Korea, many chemical accidents have occurred and affected the nearby residents' health and environment. Recently, the Ministry of Environment promulgated 'CHEMICALS CONTROL ACT' on March 2014 and came into force on January 2015. However, in this Act, soil and groundwater contamination problem during and after chemical accidents are not fully taken into account. Therefore, to manage soil and groundwater contamination in chemical accidents, we developed a framework for preliminary assessment of vulnerability to contamination of soil and groundwater.

METHODS

We reviewed several research works such as those from Ministry of Environment (2012) and NIER(2007). Then we adopted the framework scheme from Ministry of Environment (2012) which is called 'Development of national inventory system of soil and groundwater contamination source'. In the work of MOE (2012), the methodology regarding on choosing which potential source of soil and groundwater contamination should be managed prior to other sources within certain area has been developed. This methodology adopted source-pathway-receptor (SPR) concept. After scoring source, pathway, and receptor characteristics, a final score for each source is calculated applying with weights on each S-P-R characteristics. In this study, we adopted this S-P-R concept for developing a framework for preliminary assessment of vulnerability to contamination of soil and groundwater.

RESULTS AND DISCUSSION

In this study, we developed source-pathway-receptor-management (S-P-R-M) concept adding management characteristics into existing S-P-R concept. Management characteristics are related to characteristics on the degree how the source is managed properly against chemical accident. Other S-P-R characteristics are similar to the previous work of MOE (2012). Figure 1 shows the framework for preliminary assessment of vulnerability to contamination of soil and groundwater.

CONCLUSIONS

The framework proposed in this study can help regulators or policy makers to manage properly sources (or facilities) related to soil and groundwater contamination during or after chemical accidents. Furthermore, this scheme could be used for preparing related guidance on chemical accident or soil/groundwater pollution managements.

ACKNOWLEDGEMENT

This subject is supported by Korea Ministry of Environment(MOE) as "GAIA program (201400530003)"

REFERENCES

Ministry of Environment (2012) Development of soil and groundwater contamination national inventory construction method.

National Institute of Environmental Research (2007) A Study of priority management soil contamination substance selection.

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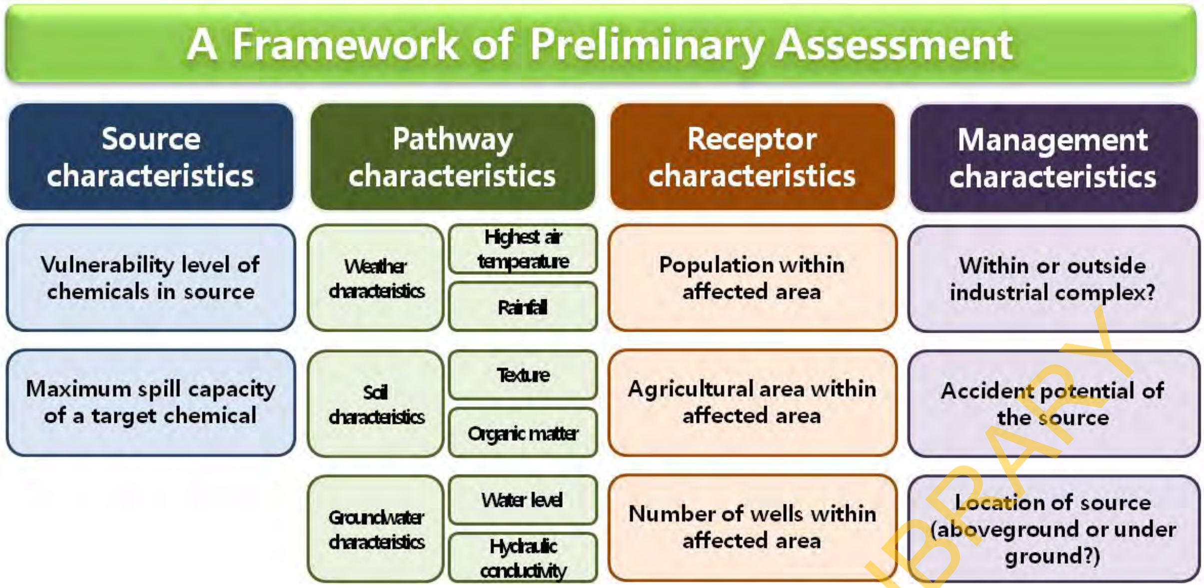

Fig. 1. **A framework for preliminary assessment of vulnerability to contamination of soil and groundwater in chemical accident**

ASSESSING ACUTE INHALATION EXPOSURE TO HYDROGEN FLUORIDE

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INTRODUCTION

A human health and toxicological risk assessment of hydrogen fluoride (HF) was undertaken for a lithium-ion battery testing facility. The objective of the works was to assess potential HF exposures to staff in the event that thermal runaway of lithium-ion battery occurs during proposed testing of the batteries. While the likelihood of this occurring was very rare and unlikely assessment to workers health was still required. The key exposure for this scenario was estimating emission rates of HF and subsequently converting these to HF indoor air concentrations. The potential release of HF for the scenario assessed involved acute exposures, seconds to minutes, and therefore obtaining appropriate short-term acute exposure standard/guidelines was the challenge. While it is more common in the contaminated land industry to undertake risk assessments where the chronic exposure is assessed this project provided the opportunity to consider the more rare acute scenarios risk assessors come across.

METHODOLOGY

The first part of the methodology was to undertake a literature review to better understand the conditions required to cause thermal runaway of Lithium-ion batteries and identify any other scenarios that may lead to potential emission of HF (e.g., short-circuiting, accidental fires etc) and to also obtain emission rates or air concentrations for HF in similar facilities/circumstances. The second step was to model the exposure scenarios, by using the exposure calculation of:

$$C = m/V \qquad (1)$$

Where, C represents concentration (C) of HF that may be inhaled, m represents the amount of HF emitted (in milligrams) and V the volume of the breathing zone (in m^3).
Three different exposure scenarios were modelled and were differentiated by the number of batteries that undergo thermal runaway:

- Scenario A – 1 cell experiencing thermal runaway with a staff member standing directly in front of it (most likely scenario)
- Scenario B - 8 cells experiencing thermal runaway with a staff member in close proximity
- Scenario C – all of the cells experiencing thermal runaway with a staff member being inside the facility (worse case and least likely scenario)
-

In selecting appropriate criteria for the modelled HF inhalation concentrations both occupational exposure limits (OELs) and emergency guidelines, including the US EPA Acute Exposure Guideline Levels (AEGLs), were considered. The US EPA (2004) AEGLs were selected given the scenario evaluated and the suitability of the averaging time. AEGLs, developed by the National Advisory Committee, are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals, which reflected the rare thermal runaway exposure being assessed in this project. The AEGLs are available for 10 minute to 8 hours exposures; however we were modelling HF exposures for 5 to 15 seconds. Therefore, time-scale downward extrapolations using Haber's Law were required. Using Haber's Law, as presented in the NHMRC (2006) 'Ambient Air Quality Standards' document, as the effect is assumed constant for a given concentration (C_1) and exposure time (t_1) product, the concentration (C_2) required to produce the same effect at exposure time t_2 can be calculated from:

$$C_1^n t_1 = K = C_2^n t_2 \qquad (2)$$

Where, K is a constant level or severity of response for a specific toxicological effect. Such extrapolation needs to be carried out carefully given the uncertainty in extrapolating large time scales (10 minute AEGL to 5-15 second exposure).

RESULTS AND DISCUSSION

The literature review identified only two appropriate studies which provided HF emissions during thermal runaway of lithium-ion batteries. As there were divergent experimental emissions rate estimates between these only two available studies the scenarios were modelled using HF emission range from both studies. Furthermore, the two studies showed that the emission rates also depended on the state of charge of the batteries, hence this needed to be incorporated for each modelled scenario which added to the complexity and range of results.

The results were presented for each of the three scenarios, for three various exposure times (5, 10 and15 seconds) and for three various state of charge of batteries (0, 50 and 100%). The results showed that AEGLs were exceeded in each scenario modelled. Therefore, given the variability in the estimated exposures and the fact that many of the estimated exposures exceed the screening AEGL extrapolated values, the potential health consequences of the exceedences required further analysis. A detailed toxicological assessment of the concentration / time response was then undertaken to characterize risks to workers. Further to this, consideration of mitigation measures was undertaken as these may aid in reducing the risks presented in the study. So for example, the use of full face respirators complying with the Australian Standard with a minimum protection factor of 50 significantly reduced the exceedance of AEGL criteria.

CONCLUSIONS

The assessment of acute inhalation exposures of HF for a lithium-ion battery using Haber's Law and US EPA AEGL values showed that staff could be exposed to health risks should thermal runaway in batteries occur during proposed testing in a facility. Combining risk assessment principles with toxicological understating of HF behavior at various time and concentration exposures and the consideration of health and safety mitigation measures allowed a more detailed assessment of the actual risks. This project was a good example for the various complexities faced with very specific and rare emergency scenarios risk assessors less routinely encounter. A sensitivity analysis and a discussion of the uncertainties was crucial to this work to better inform management of the facility using a hierarchy of controls. Understanding the contributing variables highlighted data gaps and how best these could be filled to inform greater certainty regarding the estimates of risk.

REFERENCES

NHMRC (2006). National Health and Medical Research Council. Ambient Air Quality Standards Setting – An Approach to Health-Based Hazard Assessment. Australian Government.

US EPA (2004). Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 4. Subcommittee on Acute Exposure Guideline Levels, Committee on Toxicology, National Research Council.

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COMPUTATIONAL ANALYSES ON THE INTERACTION OF MONONITROPHENOLS ON *RHODOCOCCUS WRATISLAVIENSIS* 4-NP MONOOXYGENASE

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INTRODUCTION

Nitrophenols (NPs) are toxic group of nitro substituted phenols and they are widely used in manufacturing medicines and pesticides (Kadiyala et al 1998). Their presence in the environment was documented in water, air and soil. Nitrophenols are either mono, di or tri substituted, indeed the level of water solubility decreases, from mono to tri substitution. Thus mono substituted nitrophenols are highly soluble in water and thus greatly bioavailable to the organisms. Mono substituted nitrophenols constitute *o*-NP, *m*-NP and *p*-NP and all three were equally toxic to the living organisms like plants and algae. Among the mono-NPs, PNP or 4-NP is more widely used in the industries and it is also an intermediate in the hydrolysis of pesticides like methyl-parathion (Subashchandrabose et al 2012).

Biodegradation efficiency of PNP was documented in several gram positive bacteria including *Rhodococcus* (Kadiyala et al 1998). However the role of ring cleaving 4-nitro phenol monooxygenase was not fully explored using the computational approaches. In this regard 4NP monooxygenase from *Rhodococcus wratislaviensis* an efficient degrader of 4NP was chosen for the analysis. Earlier experimental studies revealed that degradation of 4-NP by *R. wratislaviensis* was greatly affected by the presence of other NPs. Thus this study was carried out to uncover the interference of other mono NPs on 4NP degradation. *R. wratislaviensis* 4NP monooxygenase was homology modelled and used for molecular docking and simulation of all the three mono NPs.

METHODS

R. wratislaviensis 4NP monooxygenase was obtained from the whole genome sequencing of the *R. wratislaviensis* strain9 using Illumina MiSeq platform. Homology modelling was carried out using SwissModel, Molecular docking was carried out using Swissdock, quality of the model was checked using PROCHECK (Kallubai et al 2015), molecular dynamics simulation were carried out using AmberTools15.

RESULTS AND DISCUSSION

The quality check of modelled protein revealed the perfect homology model of 4NP monooxygenase using the SwissModel. Molecular docking based approaches could be reliable method for choosing an enzyme as the bioremediation tool. Docking calculations with the *o*-NP, *m*-NP and *p*-NP revealed that 4NP monooxygenase could be docked well by *o*-NP and p-NP while m-NP didn't docked well. The lower docking area (40 Å) has a impact on the docking of *o*-NP and *m*-NP, while not much interference was noted with *p*-NP. Significantly close binding energy of *o*-NP and *p*-NP shows that *o*-NP could impact the degradation of *p*-NP more than m-NP. Indeed this is in accordance with the fact that in bacteria *o*-NP and *p*-NP were degraded by monooxygenase while *m*-NP is degraded by reductase.

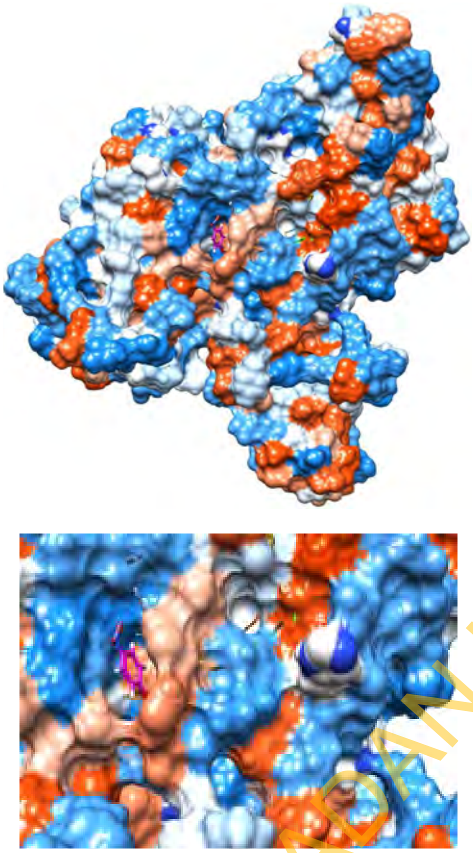

Fig. 1. PNP docked into the catalytic groove of *R. wratislaviensis* 4NP monooxygenase.

Table 1. Binding free energy (Kcal mol^{-1})

Grid Size (Å)	2 NP	3 NP	4 NP
40	-5.5	-8.12	-9.4
50	-6.4	-9.03	-9.2

CONCLUSIONS

Molecular docking and simulation studies are effective tools in analysing and predicting the enzymatic bioremediation efficacy of mixed contaminants.

REFERENCES

Kadiyala, V., & Spain, J. C. (1998). A two-component monooxygenase catalyzes both the hydroxylation of *p*-nitrophenol and the oxidative release of nitrite from 4-nitrocatechol in *Bacillus sphaericus*JS905. Applied and environmental microbiology, 64(7): 2479-2484.

Kallubai, M., Amineni, U., Mallavarapu, M., & Kadiyala, V. (2015). In silico approach to support that *p*-nitrophenol monooxygenase from *Arthrobacter* sp. strain JS443 catalyzes the initial two sequential monooxygenations. Interdisciplinary Sciences: Computational Life Sciences, 1-12.

Subashchandrabose, S. R., Megharaj, M., Venkateswarlu, K., & Naidu, R. (2012). *p*-Nitrophenol toxicity to and its removal by three select soil isolates of microalgae: the role of antioxidants. Environmental Toxicology and Chemistry, 31(9:1980-1988.

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INTERPLAY OF SOIL GAS, SOIL AND GROUNDWATER FOR CHLORINATED SOLVENT CLEAN-UP

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Background/Objectives: This paper presents the risk assessment process which was used to determine the clean-up goals, field and validation monitoring protocols from the impact of a TCE bath at a large manufacturing facility occupying several hectares in Western Sydney.

Approach/Activities: A comprehensive soil boring and monitoring well network of over 100 locations was complemented with a soil gas survey and cored boreholes to study fractured patterns within the Wianamatta Shale with gas and groundwater migration to both a first and second aquifer some 15 metres below grade. A soil gas survey at varying depths with a combination of qualitative and quantitative (suma) measurement provided more accurate data on the lateral and vertical extent of the plume associated with the TCE bath. A risk assessment utilizing equilibrium gas concentration data was then used to determine the degree of clean up required for groundwater, soil and soil gas using an integrated approach which was agreed between client, Auditor, consultant and contractor in a collaborative and cost efficient manner. The important aspect of the risk assessment process is the importance of understanding Henrys Law and Equilibrium and how this can result in an integrated decision process. This solution utilized the Tier 2 NEPM framework.

Results/Lessons Learned: Communication of risks to all stakeholders and the application of Tier 2 NEPM was the key in providing a streamlined and cost effective clean-up program which involved working closely with contractors to satisfy stakeholder objectives. An integrated risk assessment NEPM framework was used to provide a robust decision on the remediation footprint for impacted soil and soil gas with strong communication of risks. The risk assessment was able to justify that the impact of mass from groundwater was limited and did not require groundwater clean-up. Removal of TCE and daughter products was achieved by utilizing a controlled engineered soil aeration process within a warehouse environment with the use of gypsum and mechanical soil treatment techniques to deal with plastic clays. An unconditional (no EMP) Site Audit Statement was achieved.

PHYTOTOXICITY OF 2,4-DINITROANISOLE (DNAN) — AN INGREDIENT IN INSENSITIVE MUNITIONS EXPLOSIVE FILLS

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INTRODUCTION

In recent years research on DNAN is becoming prominent in the field of insensitive munitions. DNAN has become an alternative active ingredient to replace TNT in melt pourable high explosive formulations. Initially, DNAN was used industrially in the synthesis of dyes and as an insecticide in the past by the US Military (Lent et al., 2012). The environmental risks associated with the usage of DNAN on large-scale is still unclear. Walsh et al. (2014) found that high order detonation residues are slightly greater for DNAN formulation than for conventional munitions. From an environmental view point, the recalcitrant nature of nitroaromatic compounds and their toxic effects including toxic intermediate species need to be well documented and understood. Very few reports are currently available on the environmental risks associated with DNAN and further research is necessary in this area.

METHODS

Three contrasting soils were used in this study: alkaline, neutral and acidic. The top soils (0-15 cm depth) were collected, air-dried at room temperature and sieved through 2 mm sieve. The dissociation constant (K_d) of DNAN for these soils were determined. The onion and lettuce seeds were obtained commercially. They were surface sterilised by rinsing with the 95% alcohol for 10 sec and then with 10% hydrogen peroxide and 1.25% sodium hypochlorite in sufficient volumes by immersing the seeds completely for 3-5 min and rinsed with sterile distilled water for at least 10 times. Analytical grade (99% purity) DNAN was obtained from the Defence Science and Technology Organisation (DSTO), Australia. The soils were spiked with DNAN dissolved in acetone to obtain the test soil concentration of 5, 10, 25, 50, 100, 150 mg Kg^{-1}. These soils were mixed thoroughly to achieve homogeneity and were left uncovered in the fume hood until the solvent evaporated. For each plant, 10 seeds were sown in polypropylene pots containing 200g of spiked soils, watered to 60-70 % of its water holding capacity and kept in the greenhouse. Seed germination was examined by seedling emergence. DNAN induced stress on the plants was evaluated in terms of proline assay (Bates et al. 1973).

RESULTS AND DISCUSSION

Seed germination is the simple, sensitive, cost effective and rapid bioassay used extensively to evaluate acute phytotoxicity of chemicals. In the present study, the effective concentration of DNAN which inhibits 50% seed germination was analysed (Table 1). For both plants, the germination inhibition was higher in alkaline soil, followed by neutral soil and then acidic soil. The difference in the DNAN EC_{50} values in the test soils showed a clear relationship with the sorption coefficient (Kd) in soils (Table 1). Thus, the higher the Kd value the lower the toxicity to plants. Soil properties such organic carbon and clay content play a major role in sorption of DNAN in the soils which in turn influences the DNAN bioavailability.

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The accumulation of proline is a common response of the plants during the biotic and the abiotic stress conditions and plays an adaptive role in the plant stress tolerance by protecting the cells against the stress (Verbruggen and Hermans, 2008). In this study both plants exhibited the highest accumulation of the proline with the increasing concentration of DNAN in soil (Figure 1 & 2). The results indicate that the plant stress increased with an increase in DNAN concentration. DNAN decreased the growth of perennial ryegrass (Dodard et al. 2013). In this study both plants were sensitive to DNAN toxicity.

Table 1. DNAN toxicity on plant germination

Soil	Plants	Germination inhibition EC_{50} of DNAN (mg Kg^{-1})	K_d (mL g^{-1})
Acidic	Onion	67.8 (52.2 ± 80.1)	6.58
	Lettuce	62.3 (48.2 ± 76.5)	
Neutral	Onion	60.0 (54.6 ± 72.0)	3.71
	Lettuce	44.9 (33.2 ±63.0)	
Alkaline	Onion	55.4 (43.8 ± 65.5)	1.86
	Lettuce	24.6 (18.0 ± 33.9)	

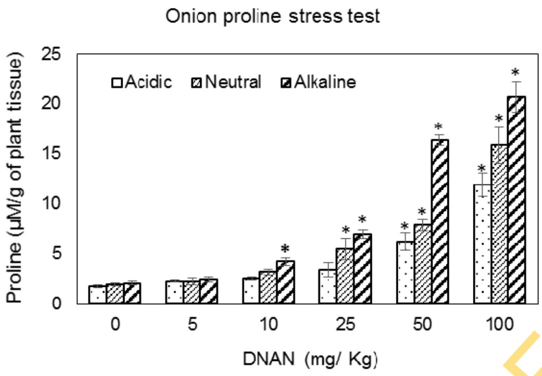

Figure 1

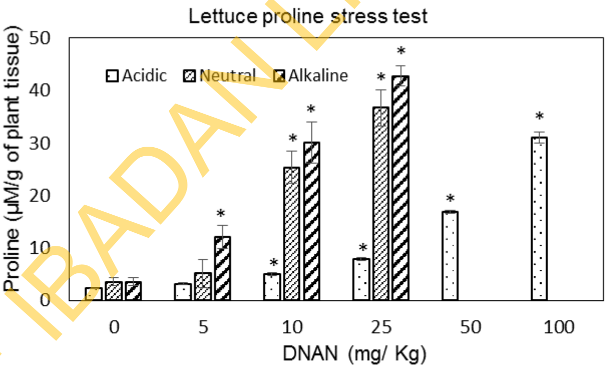

Figure 2

CONCLUSIONS

The germination and stress in terms of proline accumulation can be used to assess the toxicity of DNAN in soils. The toxicity of DNAN was influenced by soil properties. Thus the variation in the toxicity was observed between the test soils. Both plants were sensitive to proline stress test which shows DNAN exposure induces stress in plants.

REFERENCES

Bates L, Waldren RP, Teare ID 1973. Rapid determination of free proline for water-stress studies. *Plant and Soil*, 39: 205-207

Dodard, SG, Sarrazin, M, Hawari, J, Paquet, L, Ampleman, G, Thiboutot, S, and Sunahara, GI 2013. Ecotoxicological assessment of a high energetic and insensitive munitions compound: 2,4-Dinitroanisole (DNAN). *Journal of Hazardous Materials.* 262: 143-150.

Lent, EM, Crouse, LC, Hanna, T, Wallace, SM 2012. The subchronic oral toxicity of 2, 4-dinitroanisole (DNAN) in rats. Toxicology Study No. 87-XE-0DBP-10. US Army Public Health Command: Aberdeen Proving Ground, MD.

Verbruggen, N, & Hermans, C 2008. Proline accumulation in plants: a review. *Amino acids,* 35**,** 753-759.

Walsh, MR, Walsh, ME, Ramsey, CA, Thiboutot, S, Ampleman, G, Diaz, E, and Zufelt, JE 2014. Energetic Residues from the detonation of IMX-104 insensitive munitions. *Propellant Explosive and Pyrotechnic.* 39: 243-250.

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COMPARISON OF ORGANIC CHELATORS AND COMPOST-ASSISTED PHYOREMEDIATION OF A LEAD SLAG-CONTAMINATED SOIL BY *SPOROBOLUS FERTILIS* AND *GOMPHRENA SERRATE*

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INTRODUCTION

Restoration of lead smelting slag (LSS)-contaminated sites will protect soil and human health. The use of plants to remediate contaminated soil, which is termed phytoremediation has received global attention due to its low cost, less disruption to the environment and public acceptance. Plants that have been identified as hyperaccumulator for remediation of heavy metals contaminated soils were plants that grew naturally on metalliferous wastes and contaminated soils (Yanqun et al., 2005). Previous investigations on plants that colonised a site contaminated by an abandoned Pb-acid battery slag in Nigeria showed that *Sporobolus fertilis* and *Gomphrena serrate* accumulated high levels of lead (Ibigbami et al., 2014). These were selected as potential lead accumulator for possible re-vegetation and remediation of the contaminated site. Studies have shown that organic acids and composts increased heavy metals uptake by plants (Liphadzi et al., 2006). This study aimed at comparing the performance of organic chelators and composts at enhancing lead phytoremediation potential of *Sporobolus fertilis* and *Gomphrena serrate* that grow naturally on LSS-contaminated soils in Nigeria.

METHODS

In pot experiments, seedlings of *S. fertilis* and *G. serrate* were transplanted and grown on contaminated soils with composts at different rates (0, 5, 10, 15 and 20g/kg soil) and organic acids at different concentrations. Zero rate was control which was contaminated soil without amendments. 48 days after transplanting, citric acid (CA), oxalic acid (OX) and ethylenediamine tetraacetate (EDTA) at 0, 0.05, 0.1 and 0.2 M were applied. One gramme each of shoot and root was ashed in a muffle furnace for 6 hours at a temperature between 450-500°C and the ash was dissolved in 10mL of 2M HNO_3. The Pb level in the digests was determined by atomic absorption spectrophotometer (Buck scientific model 210A) with air-acetylene flame.

RESULTS AND DISCUSSION

The results of Pb uptake by *S. fertilis* and *G. serrate* grown on the untreated, compost, citric and oxalic acid solutions treated soils are presented in Figures 1-2. The two plants thrived and accumulated Pb from the untreated contaminated soil. Treatment with 20g compost/kg soil and 0.05M organic acids showed the best effectiveness at mobilising Pb for accumulation by the plants. The maximum available Pb content in the shoot, for compost, CA and OX were, 5340±43.8, 4740±8.49 and 4720±26.9mg/kg and 17900±61.5, 15400±185 and 14100±140mg/kg in *S. Fertilis* and *G. serrate* respectively. These were a few thousands higher than Pb level accumulated by plants grew on untreated soils. The acids at higher concentrations were ineffective for mobilising Pb from the soil. Citric acid, Oxalic acid and compost at appropriate proportion were all effective at improving phytoremediation of the contaminated soil by the two plants with *G. serrate* showing more promising potentials.

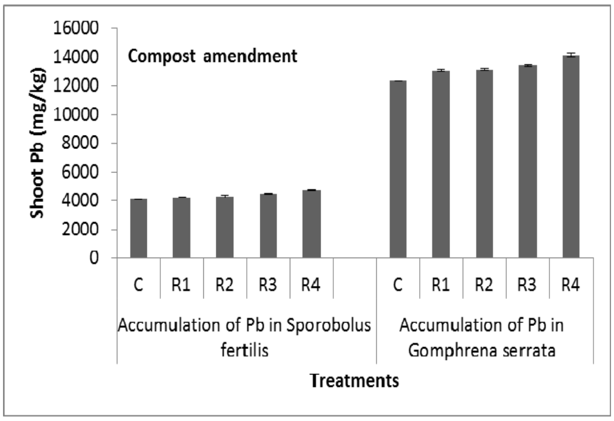

Fig.1. Accumulation of Pb in Sporobolus fertilis and Gomphrena Serrata grown on compost amended contaminated soil at different rates (Control (C) = 0g/kg, Rate (R1)= 5g/kg, Rate (R2)= 10g/kg, Rate (R3)= 15g/kg, Rate (R4)= 20g/kg)

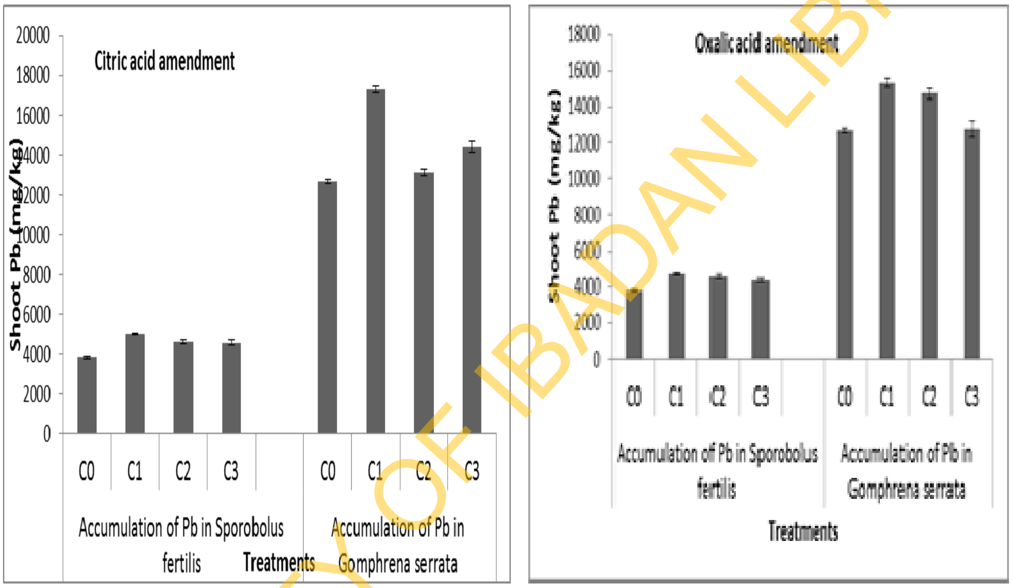

Fig. 2. Accumulation of Pb in *Sporobolus Fertilis and* *Gomphrena Serrata* grown on citric acid and oxalic acid solution amended contaminated soil at different concentrations (Control (Co) = 0M, (C1)= 0.05M, (C2)= 0.1M, (C3)= 0.2M)

CONCLUSIONS

Compost assisted *G. serrate* may be a potential accumulator to remediate lead contaminated soil. Further studies are required to improve its usefulness to remediate contaminated soil.

REFERENCES

Liphadzi, M.S. and Kirkham, M.B. (2006) Availability and plant uptake of heavy metals in EDTA-assisted phytoremediation of soil and composted biosolids. S. Afr. J. Bot. 72: 391–397

Ibigbami O. A., Ogundiran M. B. and Osibanjo O. (2014) Lead and Cadmium Phytoremediation Potentials of Plants from Four Lead Smelting Slags Contaminated Sites. Nat. Environment 2(3):33-38.

Yanqun, Z., Yuan, L., Jianjun, T.C., Haiyan, C., Li, Q., Schvartz, C. (2005) Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead–zinc mining area in Yunnan, China, Environ. Int. 31: 755–762.

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EFFECT OF WHEAT PLANT ON THE DEGRADATION OF PHENANTHRENE AND PYRENE

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INTRODUCTION

Phytoremediation, the use of plant and associated microorganisms to remove, or degrade contaminants, represents a cost effective, non-invasive technology for the clean-up of pollutants from environments. The aim of this study was to evaluate the effect of phytoremediation using wheat plant on the degradation of phenanthrene and pyrene in a spiked soil.

METHODS

An uncontaminated sandy loam was spiked with phenanthrene (500 mg/kg) and pyrene (500 mg/kg), alone or in a combination and packed into the greenhouse pots. The experiment was carried out in a greenhouse at 25-32 °C. Wheat seeds (n =5) were sown into each pot containing 1 kg of either contaminated or uncontaminated soil. The number of seedlings was thinned to three when the seedlings length was ~3-4 cm. The water holding capacity of 70% was maintained throughout the experiment. After 90 days, shoots and roots were harvested and attached rhizosphere soil and also control and clean soils were collected for further analyses. Microbial molecular tools were used as described by Shahsavari et al. (2013).

RESULTS AND DISCUSSION

The presence of wheat enhanced the degradation of both phenanthrene and pyrene. In the soil spiked with phenanthrene, the degradation rate enhanced from 97% (394 mg/kg) and 87% (392 mg/kg) for unplanted soils to 100% (406 mg/kg) and 98% (441 mg/kg) in the presence of wheat. In terms of pyerne, the degradation rate was 65% (280 mg/kg) and 70% (350 mg/kg) in planted treatments compared to 15% (65 mg/kg) and 18% (90 mg/kg) in control soils (Table 1). Microbial molecular tools showed that the presence of wheat plants led to an increase in microbial activity as well as some changes in both bacterial and fungal communities (Fig. 1).

Table 1. The degradation rate of phenanthrene and pyrene in wheat planted and control soils after 90 days of incubation.

	Treatments					
	CA	**PA**	**CB**	**PB**	**CC**	**PC**
Phenanthrene (%)	97^{b*}	100^{a}	-	-	87^{c}	98^{a}
Pyrene (%)	-	-	15^{b}	65^{a}	18^{b}	70^{a}

CA: Uncontaminated soil + phenanthrene (control)
PA: Uncontaminated soil + phenanthrene + wheat plant
CB: Uncontaminated soil + pyrene (control),
PB: Uncontaminated soil + pyrene + wheat plant
CC: Uncontaminated soil + phenanthrene + pyrene (control)
PC: Uncontaminated soil + phenanthrene + pyrene + wheat plant
* Means with the different letter are significantly different in each row at P≤0.05 using LSD test
- Not detected

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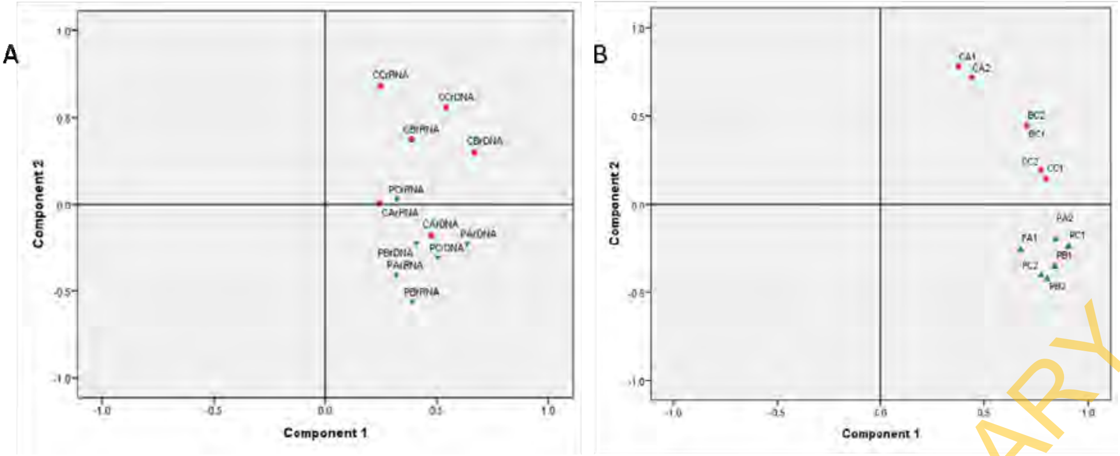

Fig. 1 Principal component analysis (PCA) on microbial DGGE profiles, total bacterial (A) and fungal (B) communities in planted and control soils.

CONCLUSIONS

Our results suggest that the use of wheat plants is an effective technique for the degradation of phenanthrene and pyrene in contaminated soils. The presence of wheat roots enhanced the microbial activity including PAH degrading organisms, possibly through the addition of root exudes and oxygen into the soils.

REFERENCES

Shahsavari, E., Adetutu, E. M., Anderson, P. A., & Ball, A. S. (2013). Tolerance of selected plant species to petrogenic hydrocarbons and effect of plant rhizosphere on the microbial removal of hydrocarbons in contaminated soil. Water, Air, & Soil Pollution, 224(4), 1-14.

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PHYTOTOXICITY OF WASTEWATER IRRIGATION

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INTRODUCTION

Global freshwater supply is considered a finite limiting resource that needs protection to ensure sustainable supply for all future generations. Thus, water resources often affected by industrial input including farm effluents (e.g. dairy effluent), is a major concern throughout the world (Dhanam, 2009; Huma, 2013). Most industries are unable to treat their waste products adequately due to the high costs involved in conventional methods. Recently, the use of industrial wastewaters for irrigation has emerged as an important treatment strategy, considering the high nutrient contents such as N, P, K, Na and Ca. However, wastewater irrigation can be both advantageous (biomass production for non-food crops) and deleterious (toxicity in food crops). This paper addresses the toxicity of various wastewater sources in the germination of a range of plant species under three different growing media (solution, sand and soil).

METHODS

Characterisation of materials used

Four different types of wastewater sources (list them) were used in this study. These wastewater sources were analysed for characteristics such as pH, EC, DO (dissolved oxygen), TDS (total dissolved solid), SAL (salinity), and ORP (oxidation-reduction potential) using Aquaread™ water quality meter.

Germination test

Onion (*Allium cepa*), maize (*Zea mays*) and sunflower (*Helianthus annuus*) were used as test plants for the germination test. The germination test was carried out using 3 growing media (list them). The wastewater sources (4mL each of raw or diluted with deionised water) were placed on glass microfiber filter (GF/A; Whatman) in 90 mm glass petridishes. The concentration of wastewater used were 100%, 75%, 50%, 25%, 10%, 5%, 0.5% and 0%. Ten seeds were placed in each dish. The dishes for each treatment were wrapped together with a polyethylene bag to prevent desiccation. The germination test was conducted over 5-7 d incubated in a dark place at 25°C temperature. Germination test was also conducted on soil and sand media irrigated with these wastewater sources. The percentage germination and radicle length were measured separately at 5d for maize and sunflower, and 7d for onion. The percent germination was calculated using Eqn.1 (Czabator, 1962). A germination index (GI) was calculated by accounting for the number of grown seeds and the average sum of seeds' root elongation in a sample as related to the control (Zucconi et al., 1981). Mean time of germination (MTG) was calculated using Eqn. 2 (Brenchley and Probert, 1998).

$$\text{Percent germination} = \frac{\text{Number of seed germinated}}{\text{Total number of seeds sown}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{GI} = \frac{\text{Number of grown seeds in sample}}{\text{Number of grown seeds in control}} \times \frac{\text{Average sum ofroot lengths in sample}}{\text{verage sum ofroot lengths in control}} \times 100 \ldots\ldots (2)$$

$$\text{MTG} = \frac{\sum(\text{n} \times \text{d})}{\sum \text{N}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where n is the number of seeds that germinated between scoring intervals, d is the incubation period in days at that time point and N is the total number of seeds germinated in the treatment.

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RESULTS AND DISCUSSION

Physico-chemical analysis of four different types of wastewater indicated very high electrical conductivity, which is a clear reflection of the high concentration of soluble salts. Winery wastewater is acidic in nature. Dairy effluent was highly turbid containing large amount of total solids. DO was very low in four wastewaters (100%), which confirms their highly polluted deteriorating condition (Table 1).

Table 1. The pH, EC and other parameters of different sources of wastewater

Wastewater Sources	Constituents					
	pH	EC (µS/cm)	DO (%)	TDS (mg/L)	SAL (ppt)	ORP (mV)
Winery WW (100%)	4.80±0.01	2001.00±15.56	3.05±0.07	1289.00±11.31	0.98±0.01	167.25±0.21
Abattoir WW (100%)	7.02±0.06	2611.00±31.11	3.65±0.07	1703.50±9.19	1.29±0.01	140.10±2.69
Dairy farm WW (100%)	8.01±0.03	6902.50±37.48	2.25±0.07	4477.50±38.89	3.46±0.01	51.15±1.48
Municipal WW (100%)	6.34±0.05	1640.00±55.15	7.70±0.14	1068.00±29.70	0.82±0.01	153.85±0.92

For each type of wastewater, the toxicity was maximum at the highest treatment as evident from slow germination of the seeds. Winery wastewater showed the highest toxic effect on germination in solution, as measured by germination test. The effect is less toxic in soil than sand and solution medium (fig. 1).

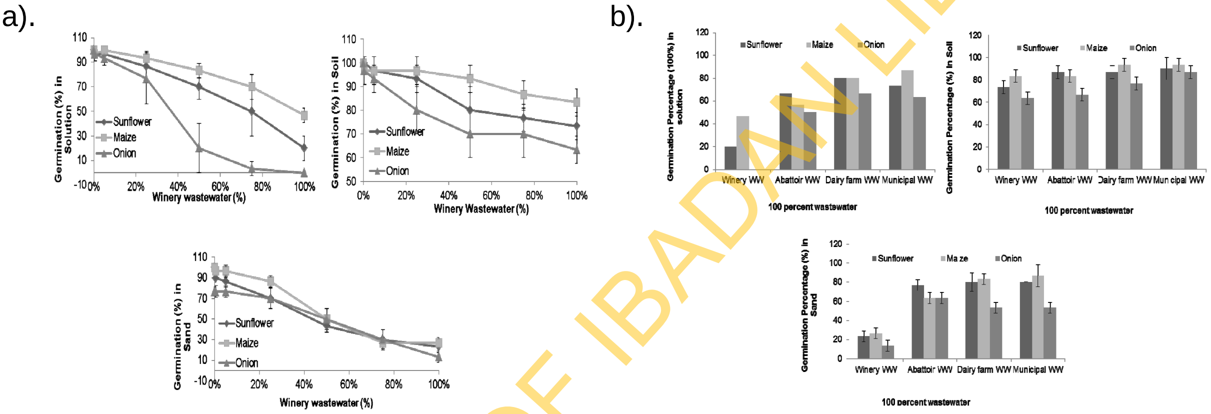

Fig. 1. Phytotoxicity of winery wastewater in solution, soil and sand to Sunflower, Maize and Onion with a). different concentration (0 to 100%) of wastewaters and b). highest concentration (100%) of wastewaters, expressed as germination percentage.

CONCLUSIONS

Present study revealed that all wastewater sources except municipal wastewater may be used after appropriate dilutions, which may enhance germination of sunflower, maize and onion. Response of various plant species to germinal toxicity was depends on both the nature and dilution of the effluent. Use of these effluents in agriculture may be a step towards water shortage solution. However, further work is required to understand the irrigational limit of these effluents on various biochemical parameters of crops.

REFERENCES

BRENCHLEY, J. L. & PROBERT, R. J. 1998. Seed germination responses to some environmental factors in the seagrass *Zostera capricorni* from eastern Australia. Aq. Bot. 62, 177-188.

CZABATOR, F. J. 1962. Germination value: an index combining speed and completeness of pine seed germination. Forest Sci. 8, 386-396.

DHANAM, S. 2009. Effect of dairy effluent on seed germination, seedling growth and biochemical parameter in Paddy Botanical Res. Internat., 2, 61-63.

HUMA, Z. 2013. Effects of domestic and industrial waste water on germination and seedling growth of some plants. Current Opinion in Agri. 1.

ZUCCONI, F., PERA, A., FORTE, M. & DE BERTOLDI, M. 1981. Evaluating toxicity of immature compost. BioCycle, 22, 54-57.

RECOVERY OF CONTAMINATED SITES IN EASTERN AND CENTRAL AFRICA, A CHALLENGE FOR A EUROPEAN CBRN-PROJECT

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BACKGROUND

Advances and industrialisation of developing countries, such as in Central and Eastern Africa (ECA), lead to increased use of all kinds of materials and substances. In the case of their accidental or malevolent release, hazardous substances may have negative impact on people and the environment. Therefore, international efforts to control and mitigate the risks which chemical, biological, radioactive or nuclear (CBRN) materials pose are growing steadily. Originally mainly focussed on weapons with CBRN materials, it is nowadays being recognised by the international community that the risks from CBRN materials are of great concern even if those are used in the general economy. In addition, the standards for handling of these materials as well as the general awareness of the dangers emanating from them are not yet fully developed in many countries.

To reduce CBRN-related risks by offering a coherent and comprehensive approach, covering legal and regulatory enforcement as well as technical issues, the European Union has put in place the CBRN Risk Mitigation Centres of Excellence (CoE) Initiative as a framework for co-operation and co-ordination between all levels of government and international partners.

PROJECT P42

The overall objective of the current (2015-2017) project '*Chemical Safety and Security in the Central and Eastern African Region*', funded as project P42 in the framework of European Union's CBRN CoE Initiative, is to enhance the sound management of chemical hazards within the ECA region by strengthening the national chemical legal framework as well as the chemical preparedness and response capabilities in the Partner Countries.

In this context, the project covers a wide scope of chemical hazard-related safety and security risk mitigation tasks:

(a) Review of the legislative and managerial systems in place concerning high risk chemicals or chemical facilities,
(b) Strengthening regional and national capacities with respect to prevention of/ preparedness for/ and response to chemical incidents,
(c) Strengthening regional and national capacities with respect to limitation of environmental consequences following a chemical incident, and
(d) Recovery measures at national level.

Point (d) plays the most prominent role in the context of contaminated sites caused by chemical incidents or inadmissible and inappropriate disposal of hazardous substances.

ACTUAL TASK

Handling of hazardous substances, e.g. in the course of their production, processing, transportation, use or disposal may always be associated with accidents which may result in long-lasting damages to the environment, even years after a release and after immediate response measures have been taken. As such, recovery refers to a broad spectrum of activities including monitoring, remediation and follow-up measures. With regard to the

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countries considered, not only technical and scientific matters need to become involved, but also the financial capacities of the countries.

Implementation of the actual task is basically intended in two steps:

(a) The development of technical guidelines for recovery measures after a chemical incident. This will cover monitoring and sampling the environment, modelling options for recovery, decontamination or remediation technologies according to technical, spatial and societal factors of the region as well as waste management (see also Table 1), and

(b) The assessment and improvement of the human capacity for recovery after a chemical incident, representing the practical application of the guidelines developed under (a). This will be achieved through workshops and training courses.

Table 1. Possible measures at a contaminated site according to German UBA.

Type of measure	Method	Follow-up
Protection Restriction	Restrictions to use Evacuation Protection against access Ventilation Interim storage of leaked substances	Investigations Safeguard measures Decontamination measures
Safeguards to interrupt transfer of pollutants	Passive hydraulic and pneumatic measures Encapsulation measures Immobilization	Monitoring Repair Re-measure
Decontamination	Active hydraulic and pneumatic measures Chemical-physical treatment Biological measures Thermal treatment	Disposal of residues Monitoring Re-measure
Relocation	Excavation Relocation to licensed landfill	Monitoring of the landfill

This year's CleanUp conference will help to ensure that all current developments in this field are taken into account while developing respective guidelines and training programs for the individual Partner Countries in the ECA region.

ACKNOWLEDGEMENTS

Project P42 is based upon the Service Contract for European Union External Actions N^{o} IFS/2014/346-488. Beside GRS, the European Consortium consists of a) ENCONET Consulting Ges.m.b.H. (Austria), b) SCK•CEN (Belgium), c) the Institute of Industrial Organic Chemistry IPO (Poland), and the Federal Office for Economic Affairs and Export Control BAFA (Germany). The African Partner Countries in the ECA region are Burundi, Democratic Republic of Congo, Ghana, Kenya, Republic of Seychelles, Rwanda, Tanzania and Zambia.

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EVALUATING SUPER OXYGENATED WATER (SOW) INJECTIONS AS A VIABLE REMEDIATION TECHNOLOGY — SOW INJECTION TRIAL

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INTRODUCTION

Super oxygenated water (SOW) injection is an emerging groundwater remediation technology targeting dissolved phase hydrocarbon impacts. Injecting high concentrations of dissolved oxygen (DO) into the aquifer stimulates in situ biological degradation of groundwater and capillary fringe organic impacts, and therefore, accelerates the remediation process of degrading hydrocarbons. The assessment results provide an insight into the processes involved in determining whether SOW injection is a viable, site specific remediation option – results of two SOW injection trials completed in Victoria have been reviewed, one in fractured basalt and the other in clayey sands.

SOW TRIAL OBJECTIVES

A SOW injection trial evaluates if the proposed groundwater remediation technology is applicable to the site, by providing information on:

a) the response of the aquifer to the water injections
b) the effectiveness of SOW injections to stimulate biodegradation and therefore accelerate the remediation process

SOW TRIAL METHODOLOGY

A SOW injection trial is undertaken in two stages and comprises the following scope of works:

Stage 1 - Step injection test

A hydrogeological assessment is undertaken to evaluate the response of the groundwater aquifer under imposing hydraulic stress. Mains water (not saturated with oxygen) is injected into a groundwater well (injection well) at stepped increments to assess the optimal rate of injection. The optimal injection rate is assessed based on the area of groundwater influence, in particular the influence on surrounding monitoring wells and groundwater level stabilisation in the injection well.

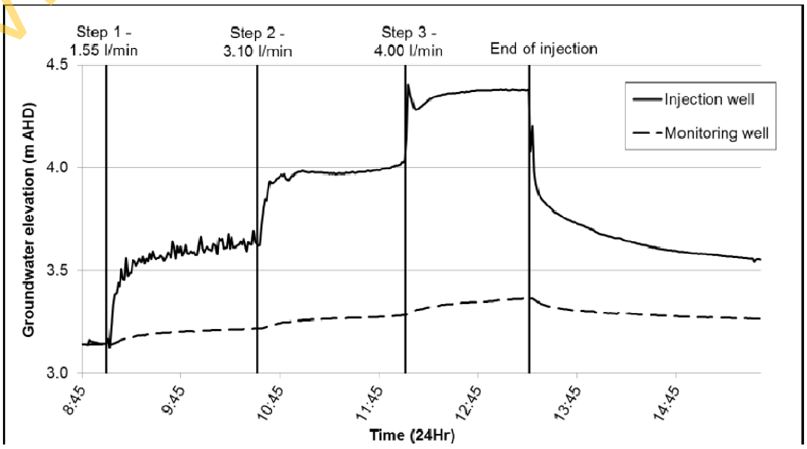

Fig.1. Step 1 – Step Injection Test. Groundwater elevation (m AHD) versus Time (24Hr)

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Stage 2 – SOW injection test

SOW is injected into the hydrocarbon impacted aquifer at the optimal rate over an 8 week period (based on results from Stage 1). Dissolved oxygen is injected into the aquifer at concentrations of greater than 40 mg/L.

RESULTS AND DISCCUSSION

Data collection through a range of monitoring activities is completed to generate lines of evidence to assess the effectiveness of the SOW injection.

Groundwater Elevations

Groundwater levels are measured through manual gauging and dataloggers to assess baseline conditions and monitor changes in groundwater following injection of SOW. A comparison between static groundwater conditions and measurements taken during SOW injection enable the injection area of influence to be defined.

Chemicals of interest (COI) concentrations

Groundwater chemistry monitoring is conducted to assist with evaluating the effectiveness of SOW injection to enhance natural attenuation and remediate dissolved phase hydrocarbon impacts.

Measuring the chemicals of interest (COI) concentrations (i.e. benzene and total recoverable hydrocarbons (TRH)) in groundwater enables a direct assessment of the SOW injection influence by measuring concentration change. Measurements are taken from monitoring wells within close proximity to the SOW injection locations, both up and down gradient.

Enhanced Natural Attenuation (ENA) Parameters

Field based groundwater physio-chemical parameters (DO, redox, nitrate, sulphate, ferrous iron and quantitative polymerase chain reaction (qPCR)) are monitored to assist with understanding aquifer conditions in particular those which enable the processes required for in situ biological degradation of hydrocarbon impacts in groundwater.

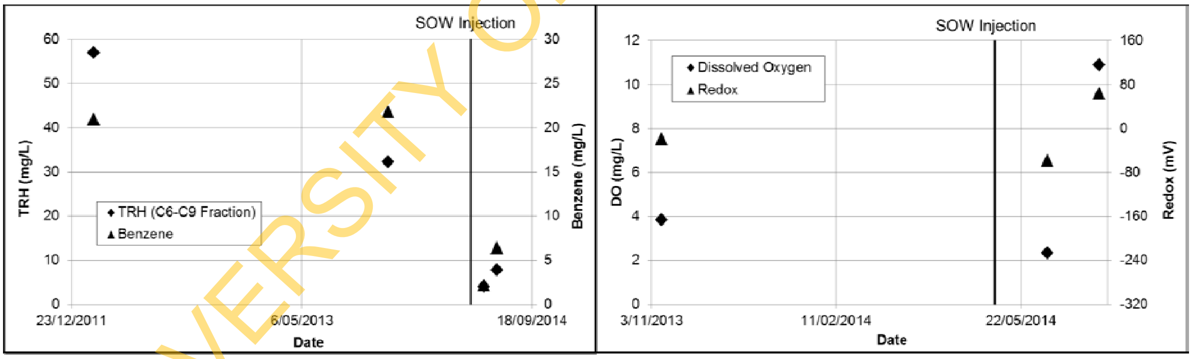

Fig.2. COI concentrations and ENA parameters measured at a monitoring well down gradient of SOW injection

CONCLUSION

SOW injection trials determine whether SOW may be implemented as a site specific remediation technology used to target groundwater hydrocarbon impacts. The trial provides guidance for full scale remediation system design and operation settings should SOW be employed.

LAND REMEDIATION: IS RADIOACTIVITY AN ISSUE?

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INTRODUCTION

Radiological surveys for land remediation projects are not straightforward to undertake. There is limited Australian guidance documents on which to base the radiation monitoring and sampling strategy as well as radiation legislation varies across Australian state and territory jurisdictions. The radiation consultant develops a strategy from known historical use information of the land and an initial walk-through inspection of the site. The purpose of the strategy is to identify whether historical use of the site has contributed to ambient radiation dose rates and soil activity concentrations above natural background levels for the local area. Individual ambient gamma-ray dose equivalent rate measurements are undertaken at a height of approximately 1 metre above ground level. The survey is performed in an approximate grid pattern with several measurements recorded at each designated point and averaged. The density of the grid is dependent on expected dose rates and levels of variability.

On completion of the dose rate survey, soil samples are collected from across the study area. The sample locations are determined from the results of the external gamma-ray survey. Depending on the situation, consideration is given to sampling at depth.
Gamma-ray spectrometry is the most common method to determine the activity concentrations of naturally-occurring radionuclides or radioactive waste products in soil. This technique is commonly used for the analysis of solids and liquids for low levels of gamma-emitting radionuclides because it is a multi-nuclide and, essentially, a non-destructive measurement method. The activity concentrations within the soil are compared with International Atomic Energy Agency (IAEA) regulatory guidance to identify if the material is of regulatory concern from a radiological perspective.

The information about the radiological characteristics of the soil as well as the gamma-ray dose rate survey are used to model estimates of prospective doses that may be received by remediation contractors, future users of the land as well as those persons who occupy neighbouring properties. The prospective doses are compared with legislated annual radiation dose limits or local regulatory dose constraint.

CASE STUDY

A case study for conducting a radiological survey of a site for remediation is presented. The case study includes, for example, selecting appropriate radiation monitoring equipment, identification of sampling locations and the prospective estimated doses to the public and workers from potential radiation exposure scenarios.

MICROALGAL BIOMASS PRODUCTION AND PIGGERY WASTEWATER REMEDIATION — USING THE SOIL ISOLATES OF *CHLAMYDOMONAS* SP. AND *DESMODESMUS* SP.

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INTRODUCTION

Microalgae are promising candidates for removing nutrients from wastewater with simultaneous biomass production for biodiesel. Nutrients like nitrogen and phosphate are the major pollutants in the waste water released from most of the agricultural industries including piggery. In Australia, the pig industry alone generates a volume of ~275,000L of wastes from ~ 15,000 pigs (800 t) in a day. The nutrient released along with the waste water goes unused. It also poses severe ecological hazards if it is released untreated into the fresh water streams. Waste water rich in carbon, nitrogen, phosphorous and other minerals are suitable nutrient sources for the growth of various algae. Combining wastewater remediation with algal biomass production is one of the most economical and environmentally sustainable ways to produce biodiesel and bio-products. In this study, growth, lipid accumulation and nutrient removal by *Chlamydomonas* sp. and *Desmodesmus* sp. in piggery wastewater was determined.

METHODS

The soil microalgae *Chlamydomonas* sp. and *Desmodesmus* sp. isolated from South Australia were used for the study and maintained in Bold's basal medium. Batch experiment was carried out using pre-treated piggery wastewater with 80% dilution of ultrapure water as a growth medium for algae (Ji et al., 2012). The concentration of chlorophyll was used to determine the growth rate of *Chlamydomonas* sp. and *Desmodesmus* sp. The chlorophyll concentration was calculated using formulas derived by Lichtentaler and Wellburn (Sükran et al., 1998). Lipid accumulation and morphological studies of individual cells were done by using Agilent Technologies Cary 600 series Fourier transform infrared spectrometer (FTIR) and Nile red method using Olympus BX41 Fluorescence microscopy (Dean et al., 2010). Total nitrogen and phosphorous were determined using Shimadzu Total nitrogen measuring unit and DIONEX ICS - 2000 Ion chromatography system.

RESULTS AND DISCUSSION

After an incubation of 4 weeks at 24°c, figure.1. shows a decrease in total nitrogen from 184.24 mg/L to 16.7 mg/L and 175.45 mg/L to 9.8 mg/L in *Chlamydomonas* sp. and *Desmodesmus* sp. respectively. Results show removal of phosphate from 25.8 mg/L to 14.31mg/L and 25.98mg/L to 19.4mg/L in *Chlamydomonas* sp. and *Desmodesmus* sp. respectively after 4 weeks of incubation. From table.1, different phases of algal growth from lag phase to death phase from week 0 to week 4 with an increasing concentration during stationary phase (week 3) is shown. Fluorescence microscopy images shows an increased accumulation of lipids and FTIR spectrum provides the presence of lipid band at 1742 cm^{-1} in both *Chlamydomonas* sp. and *Desmodesmus* sp. after an incubation of 4 weeks. Lipid content was determined using the ratio between amide(1655 cm^{-1}) and lipid(1742 cm^{-1}) bands(Dean et al., 2010).

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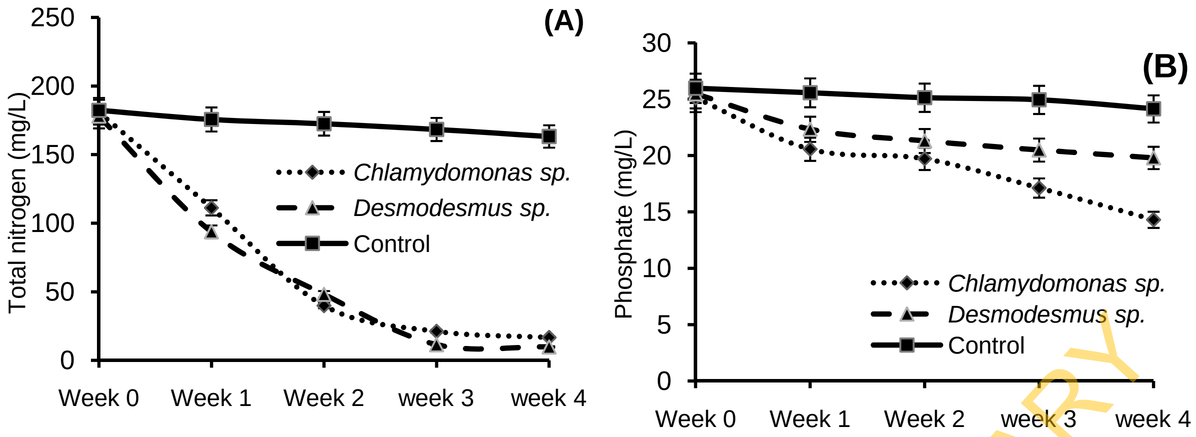

Fig.1. (A) Total nitrogen and (B) phosphate removal in pre-treated piggery wastewater by *Chlamydomonas* sp. and *Desmodesmus* sp. from week 0 to week 4

Table.1. Growth rate of *Chlamydomonas* Sp. and *Desmodesmus* sp. using Chlorophyll contents – Chlorophyll A and B.

Total chlorophyll (µg/ml)	**Week 0**	**Week 1**	**Week 2**	**Week 3**	**Week 4**
***Chlamydomonas* sp.**	0.99459	2.83464	2.21454	7.49763	1.80345
***Desmodesmus* sp.**	1.17057	2.15736	2.52459	5.40027	2.15736

CONCLUSIONS

This research shows microalgal species: *Chlamydomonas* and *Desmodesmus* can grow efficiently in pre-treated piggery wastewater and can accumulate lipids which can have a potential in effectively utilizing nutrients to increase the biomass production with higher lipid accumulation for biodiesel production.

REFERENCES

DEAN, A. P., SIGEE, D. C., ESTRADA, B. & PITTMAN, J. K. 2010. Using FTIR spectroscopy for rapid determination of lipid accumulation in response to nitrogen limitation in freshwater microalgae. *Bioresource technology,* 101**,** 4499-4507.

JI, M.-K., KIM, H.-C., SAPIREDDY, V. R., YUN, H.-S., ABOU-SHANAB, R. A., CHOI, J., LEE, W., TIMMES, T. C. & JEON, B.-H. 2012. Simultaneous nutrient removal and lipid production from pretreated piggery wastewater by *Chlorella vulgaris* YSW-04. *Applied Microbiology and Biotechnology***,** 1-10.

SÜKRAN, D., GÜNES, T. & SIVACI, R. 1998. Spectrophotometric determination of chlorophyll-A, B and total carotenoid contents of some algae species using different solvents. *Tr. J. of Botany,* 22**,** 13-17.

BIOMASS PRODUCTION AND NUTRIENTS REMOVAL BY A NEW ALGAL STRAIN

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INTRODUCTION

With the increasing global energy need and the depleting petroleum resources, algal biofuels have been proposed as a potential renewable fuel for a long time. However, the fast diminishing resources, freshwater, and high cost of nutrients have increased the cost of algal biomass production.

Thus, it is essential to find alternative resources of water and nutrients for large scale cultivation of algae. The best option is to choose wastewaters which are rich in organic and inorganic nutrients. Recently, many studies have focused on algal biomass production using municipal sewage wastewater, artificial wastewater, industrial wastewater, agricultural wastewater, and so on (Rasoul-Amini, Montazeri-Najafabady et al. 2014). The results showed that algal biomass production could be considered as a good technology for wastewaters remediation. The wastewaters were diluted to a low nutrient concentration for algal biomass production (Ji, Liu et al. 2014). The present studies were aimed to investigate the utilization of wastewaters with high nutrient concentration as growth media for cultivating algae.

METHODS

Algae Identification and Cultivation

A new algal strain was selected and purified by plate streaking in Bold's basal medium agar. The axenic cultures of the new algae were grown in 100 ml BG-11 medium in a 250 ml council flask, incubated in a constant temperature room at 24 ºC under light/dark cycles of 14:10 h for 1 week. The algal biomass was harvested by centrifugation. And, the cell pellets were directly used for DNA isolation. Algae was identified based on 18S rRNA gene sequences (Krishnamurti, Subashchandrabose et al. 2013).

Wastewater Collection and Characteristic

The dairy wastewater and winery wastewater were collected from dairy farm and winery industry in South Australia. The large solid particles were removed by sedimentation and filtration with filter cloth. The filtered wastewaters were stored in cold storage (<4.0 ºC) until its use in the experiments. The characteristics of the two types of wastewaters are summarized in Table 1. The dairy wastewater contains relatively high levels of nutrients, whereas, the total ammonia and total nitrogen in the winery wastewater are very low.

Experimental procedures

Batch experiments were carried out in 250 ml council flasks with 100 ml working volume. In order to examine the utilization of nutrient-rich wastewaters for algal growth, the 33% dairy wastewater and 50% winery wastewater were used as algal growth media. The flasks inoculated with 10% (v/v) stock algal culture were kept in the shaker at 95 rpm rotation speed. After every 48 h, samples were withdrawn for the analysis of chlorophyll content and nutrient removal.

RESULTS AND DISCUSSION

(a) The phylogenetic analysis indicated the new algal strain has a close relationship with *Diplosphaera* sp..

(b) The nutrient removal from dairy wastewater and winery wastewater by *Diplosphaera* sp. are shown in Fig.1. After 14 days, the COD concentration was reduced from 2020 and 2093 mg/L to 509 and 337 mg/L in 33% dairy wastewater and 55% winery wastewater, respectively. This higher COD removal efficiency in winery wastewater could be attributed to its lower concentration of TP, TN and TAN. The tendency for nutrient removal in both wastewaters was similar. And, the residual nutrient concentrations were suitable for reuse as irrigation water (Prajapati, Choudhary et al. 2014).

(c) The biomass productivities of *Diplosphaera* sp. under different wastewaters were also investigated. For dairy wastewater, the new algae grew slowly in first few days, and then, the growth rate became rapid. In contrast, the new algae grew faster in winery wastewater. After 14 days, the chlorophyll contents of the new algae cultivated in 33% diary wastewater and 50% winery wastewater reached to 30.4 and 15.2 mg/L, respectively. The results indicated that high nutrient concentration (TN, TP and TAN) could make algae grow slowly. However, the algal biomass productivity could be limited by the low nutrients concentration.

Table 1. Characteristic of wastewaters

Characteristics	Dairy wastewater	Winery wastewater
pH	7.36	5.66
EC (ms)	5.16	1.75
COD (mg/L)	5562.64	4348.43
TN (mg N/L)	284.75	7.67
TP (mg PO_4^{3-}-P/L)	77.94	21.78
TAN (mg/L)	200.25	1.46

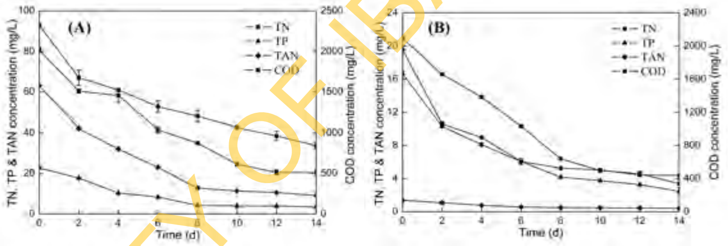

Fig. 1. Changes of nutrient concentration in dairy wastewater (A) and winery wastewater (B)

CONCLUSIONS

The new algae, *Diplosphaera* sp. should have great potential for its application in remediating wastewater. The highest algal biomass production was observed at 33% dairy wastewater after 14 days cultivation.

REFERENCES

Prajapati, S.K., Choudhary, P., Malik, A., Vijay, V.K. (2014) Algae mediated treatment and bioenergy generation process for handling liquid and solid waste from dairy cattle farm. *Biores. Tech.* 167:260-268.

Ji, F., Liu, Y., Hao, R., Li, G., Zhou, Y.G., Dong, R.J. (2014) Biomass production and nutrients removal by a new microalgae strain *Desmodesmus* sp. in anaerobic digestion wastewater. *Biores. Tech.* 161:200-207.

Krishnamurti, G.S.R., Subashchandrabose, S.R., Megharaj, M., Naidu, R. (2013) Assessment of bioavailability of heavy metal pollutants using soil isolates of *Chlorella* sp. *Environ. Sci. Pollut. Res.* 1-7.

Rasoul-Amini, S., Montazeri-Najafabady, N., Shaker, S., Safari, A., Kazemi, A., Mousavi, P., Mobasher, M.A., Ghasemi, Y. (2014) Removal of nitrogen and phosphorus from wastewater using microalgae free cells in bath culture system. *Biocata. Agric. Biotech.* 3:126-131.

PATAWALONGA SEDIMENT MANAGEMENT WORKS 2015

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INTRODUCTION

The Patawalonga Lake System (PLS) located in Adelaide is designed to circulate sea water through the lake regularly and divert storm water flow from the upper catchments to the sea. Sediment accumulation is an on-going issue and requires management to ensure the water quality of the lake, the aesthetic quality of the surroundings and mitigate the sediment load from the PLS to the Gulf St Vincent. Previous works and investigations have shown that the handling and disposal of sediment dredged from the PLS is difficult to manage due to its physical and chemical characteristics, including a high proportion of organic matter in various states of decomposition, hence the material does not fully 'drain' under gravity and can take years to dry. The material also contains elevated concentrations of total petroleum hydrocarbons (TPH) and heavy metals, thereby constraining re-use options.

In 2014 Enviropacific undertook the dredging and mechanical dewatering of approximately 15,000 m^3 of sediment from Basin A and the Diversion Basin using technologies typically utilised by the oil and gas industry for dewatering drilling muds. The sediment required dewatering to allow transport and disposal offsite for beneficial re-use. Recently Enviropacific undertook the dredging and dewatering of approximately 10,000 m^3 of sediment from Basin A and Basin B, this time utilising geotextile tube technology.

METHODS

The accumulated sediments were removed via a cutter suction dredge and pumped via a floating pipeline over a maximum distance of 350 m to the treatment area. Prior to discharge into the geobags within the treatment area, a polymer was added via a dosing pump to release the water phase from the sediment. The material then flowed into the geobags, which caught and dewatered the sediment with the resulting clear water returning by gravity to Basin B. Once filled, the bags were left to rest to allow further dewatering.

RESULTS AND DISCUSSION

The presentation will provide an overview of the works including operational details, challenges and results.

CONCLUSIONS

Successful dewatering of the stormwater sediments contained within the PLS was achieved utilising polymer addition and geotextile tube technology. The end product was a spadeable material which was able to be loaded and carted offsite in road trucks for processing and subsequent beneficial re-use.

ASSESSMENT OF BURNT CCA TIMBER RESIDUE IN THE GRAMPIANS NATIONAL PARK

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INTRODUCTION

Bushfires in the Grampians National Park in February 2013 and January 2014 resulted in the combustion of treated timber structures containing copper, chromium and arsenic (CCA). The residual concentrations of CCA in ash residues and soil at six sites were assessed approximately one year following the fires. Prior to the assessment works, all partially burnt CCA timber structures were removed from the area. Some bollards and fence posts had been burnt to or below the ground surface, leaving visible ash and discolouration.

The focus of the assessment was the post fire distribution of the CCA contaminated ash residues and soil, potential health risks and practicability of effecting clean-up.

METHODS

Rapid and cost effective collection of semi-quantitative data on the vertical and spatial distribution of CCA containing ash residues and soil was achieved using a hand-held X-Ray Fluorescence (XRF) analyser. High resolution measurement location accuracy was achieved using a Trimble 6000 Global Positioning system (GPS) referencing the *VICPos* permanent GPS reference stations, providing real-time decimetre accuracy. Georeferenced aerial photographs and where available survey plans were used to identify the former structure locations.

At each CCA former timber structure location, the XRF analyser was used to measure the CCA concentrations within the soil profile. Initial delineation measurements were located approximately 0.5 m in each of four directions surrounding the structure. Where CCA concentrations exceeded investigation levels, measurements were 'stepped out' approximately 1 m beyond the initial location in that direction until the concentrations measured were below the adopted investigation levels. CCA concentration measurements were recorded at 1,386 locations in total. 13 soil samples were also collected for laboratory analysis to compare the XRF results with laboratory determined CCA concentrations. To vertically delineate the CCA concentrations, the surface soil at selected locations was scraped back in approximately 10 mm lifts to record CCA concentrations at varying depths.

National Environment Protection Measure (NEPM) (NEPC, 2013) health investigation levels (HILs) for public open space were adopted to assess health risk at the sites. Site specific HILs for arsenic and copper were subsequently derived using the NEPM methodology.

RESULTS

The field surveys identified clear trends in rapidly decreasing CCA concentrations in surface soils at increasing distance from the former structures. Higher concentrations were recorded around larger structures where the mass of CCA would obviously have been greater. However, no consistency was observed in the distribution of CAA contamination around particular types of burnt structures. Contamination was generally delineated horizontally to within a 0.5 m radius of most structures, although sometimes extending further in a dominant direction inferred to be due to the prevailing wind conditions at the time of the fire or in areas where ash residue was washed into and concentrated particular areas. Impacts rarely extended more than 1.5 m from structures. In areas where the topsoil contained relatively higher amounts of organics material, elevated CCA concentrations were measureable up to

7 m from the bunrt structures. The higher concentrations of CCA measured in lower lying areas is expected to be due physical transport processes combined with lower mobility expected due to the generally higher organic content of the topsoil.

CCA contamination was vertically delineated to within a maximum depth of 2-3 cm below the surface, with the exception of particular areas where CCA was concentrated in natural hollows or in areas of sediment build up (former steps). Resulting from the burnt timber removal, the highest overall CCA concentrations were recorded in ash/charcoal piles which often displayed green copper discolouration. Due to the elapsed time between the fires and the field survey, relatively higher concentrations were found in areas sheltered from wind or rain such as beneath overhanging rock formations.

Arsenic concentrations exceeded the adopted HILs at three of the six sites, and at only five locations. Chromium exceeded the HIL at one location at one site, as shown in the Table 2 below which summarises the overall CCA results and exceedances across the six sites.

Table 2. Summary of CCA concentrations recorded at each site.

No of Locations	Chemicals	Max concentration (mg/kg)	No. of HIL Exceedences
1,386	Arsenic	27,412	5
	Copper	59,477	-
	Chromium (III)	179,022	1

The variables affecting the distribution of the CCA concentrations were inferred to include:

- Soil type - harder/compacted soils displayed less leaching or mixing through the soil profile compared to loose sand and soils with higher organic content displayed higher CCA concentrations.
- Whether the site was sheltered, reducing effects of wind/rain from dispersing the CCA residue away from the source over time.
- Initial concentrations of CCA used to treat timber structures as shown by different ratios of CCA at different sites.
- Elapsed time since the fire, allowing residues to disperse laterally (and vertically).

Some variation between the XRF measurements and laboratory determined concentrations was expected due to the heterogeneous nature of soils (e.g. charcoal fragments), combined with the relatively larger sample collected for laboratory analysis compared to the XRF measurement area at the soil surface. The XRF measurements were generally within the same order of magnitude and showed the same variation/patterns within the sample population as the laboratory results, therefore the XRF measurements are considered to be within the range expected and were considered valid for the assessment purpose.

CONCLUSIONS

The risk of adverse health effects due to the limited extent of CCA residue at these sites was assessed to be low and acceptable. The bulk of the CCA impacts at the sites after approximately 1 year following the fires were most commonly limited to within 0.5 m of the former timber structures. A practicable measure identified to reduce risks from the CCA residue in the future included collecting and removing the concentrated CCA ash residue at the site as soon as possible after the fire, thereby limiting its dispersal and the volume of affected soil.

REFERENCES

NEPC (2013). *National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013 (No. 1),* Canberra: National Environment Protection Council.

MULTI-DISCIPLINARY APPROACH TO A COMPLEX REHABILITATION

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INTRODUCTION

The rehabilitation of a Borrow Pit required a multi-disciplinary approach to determine the best option that key stakeholders including SA Water and Defence could agree upon.
Various investigations, including contamination, hydrogeological, geo-technical, bio-solid, and ecological were undertaken to assess the current status of the site, its biodiversity and the interconnectivity between site ponds with local and regional groundwater. Based on the results of these investigations an option to infill the Borrow Pit using site won material and restore native vegetation was developed and implemented.

BACKGROUND

The site is located within the Murray Bridge Waste Water Treatment Plant Wetlands site, itself part of the Murray Bridge Training Area (MUTA), which is a Department of Defence administered Army Field Firing Range and Training Area. It consisted of three major ponds (A, B and C) from which water is used for irrigation at the firing range, as well as for a commercial piggery, located approximately 3 km south of the MUTA wetlands. The wetlands are also an important habitat for native fish, yabbies and birdlife.
The Borrow Pit was approximately 80m in diameter and 9m deep at its deepest, and was part of the unused portion of Pond A. Surrounded by local limestone rock, it contained water that infiltrated through from the neighbouring Pond B and contained effluent waste. Prior to rehabilitation various environmental concerns needed to be assessed including the biosolids grading and whether once settled out within the Pit, they migrated horizontally through preferential pathways in soil or vertically to the regional aquifer groundwater. There were also hydrogeological issues regarding interconnectivity between the perched and regional aquifer. Odour, insects, legislative compliance with EPBC Act, geotechnical, revegetation and visual amenity also required investigation to ensure that rehabilitation would not create an unacceptable risk to the environment and or human health.

MULTI-DISCIPLINARY INVESTIGATIONS

GHD implemented a staged approach to assessment that included understanding the site history, determining the potentially contaminating activities (PCA's), and then collecting biosolids, groundwater and surface water samples to determine whether actual contamination existed. Six shallow groundwater monitoring wells were sampled to assess the perched aquifer and a deeper regional groundwater monitoring well that was installed to approximately 55mbgs was used to assess the potential interconnectivity between perched groundwater in the Borrow Pit that may be leaking into the regional aquifer. A review of the drillers logs to further refine the Conceptual Site Model and determine whether the underlying clay aquitard had potentially been compromised was also undertaken. Surface water samples were also collected from the Borrow Pit and Pond B and all water samples were analysed for the contaminants of concern (metals, nutrients, alkalinity, major anions/cations). The hydrogeological analysis included the generation of stiff diagrams, piper plots and radial plots which in conjunction with contaminant assessment was used to assess the potential interconnectivity between aquifers.

Seven biosolids samples were collected from the Borrow Pit sludge and used to assess the biosolids grading based on stabilisation and contamination grading. The fill material surrounding the Borrow Pit was assessed for geotechnical suitability to be used as backfill material. This was important to determine otherwise a significant volume of imported fill would be required, which may have been cost prohibitive to the project.

An assessment of site ecology, including EPBC listed species, was undertaken to determine the likely impacts of rehabilitation on local flora/fauna populations.

In addition, unexploded ordinance (UXO) needed to be assessed as a potential hazard during earthworks, given that a portion of the site was used as a firing range.

RESULTS AND DISCUSSION

UXO

A map of UXO risk areas for the site clearly indicated that the Borrow Pit and surrounding ponds were a low risk area. Although live firing occurs on the base, there was not expected to be any UXO in the vicinity of the Borrow Pit during rehabilitation works.

Geotechnical Results

Use of the site-won fill material was one of the options put forward based on the material being local and therefore of similar type, suitable for backfill with consideration of dewatering prior to placement which may result in mud-waving.

Biosolids Results

Sampling of the biosolids at the edge of the Borrow Pit classified the biosolids as contamination Grade B and Stabilisation Grade B resulting in an overall classification of Grade B biosolids. The biosolids were reported as having low salinity levels, a pH slightly basic (which is considered an advantage in applying to Australian soils), and relatively high nitrogen and phosphorus concentrations, which provides some benefit for agricultural applications. Multiple Extraction Procedure (MEP) results for leachate reported non-leaching of metals from the biosolids material. Based on the above the biosolids were suited to disposal applications including site rehabilitation.

Groundwater, Surface Water and Hydrogeochemical Results

The shallow groundwater and surface water samples generally reported concentrations below NEPM GILs. The deeper groundwater well reported concentrations of F, TKN and P that vary from the concentrations of these analytes in the perched aquifer and Borrow Pit water. This indicated that the regional aquifer and perched aquifer are not likely to be mixing. In addition, the deeper well was logged as having more than 20 metres of clay underlying the top layer of calcrete/sand. This provided another line of evidence that interconnectivity between aquifers would be unlikely.

Ecological Significance

The wetlands are an important habitat for native fish, yabbies and birdlife, as identified from previous bird and aquatic surveys. Site rehabilitation with appropriate planting would enhance this ecosystem.

CONCLUSION

The results of the investigations progressively resolved concerns relating to contamination, biosolids grading, aquifer interconnectivity, and suitability of the fill. This enabled rehabilitation options to be developed. It was agreed by key stakeholders, based upon the level of risk identified, that the option to use the imported fill material surrounding the Borrow Pit and grading the slopes to meet the current Borrow Pit crest line was the best approach. A revegetation plan was developed to ensure planting would support the local ecology. This work commenced following agreement between SA Water and Defence, and the Borrow Pit was backfilled following dewatering during the summer of 2014/2015. Revegetation of the Borrow Pit is planned for autumn 2015 and should see a successful conclusion to this complex rehabilitation.

REMEDIATION OF PCB IMPACTED SOIL

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INTRODUCTION

Enviropacific were engaged to remediate a former transformer manufacturing facility located in Preston, Victoria (the Site). Historical site activities included the use of Polychlorinated Biphenyls (PCB), chlorinated solvents and petroleum hydrocarbons ('TPH'). Sections of the concrete hardstand, underlying soil and rock along with the groundwater were predominantly contaminated with PCB congeners, trichloroethene (TCE), TCE degradation products (cis-1,2-dichloroethene, DCE, and vinyl chloride, VC) and TPH in the C_{10}-C_{36} range. All works were undertaken by Enviropacific in accordance with the relevant State and National Laws and the site specific PCB Environment Improvement Plan (PCB EIP).

The goal of the remediation works was to remediate the Site so that the remaining soil and/or hardstand were 'PCB free' (as defined by the Notifiable Chemicals Order for PCB (NCO) [Victoria Government Gazette No. S 5 Tuesday 1 February 2000]. This involved removing all material that was categorised as Non Scheduled or Scheduled PCB waste to ensure that any chemicals in the remaining soil do not pose unacceptable risks to groundwater or the on-going commercial/industrial use. Pre-classification of the hardstand and underlying soils was undertaken by the Environmental Consultant prior to mobilisation, with 35 PCB impacted layers/zones and 12 unclassified layers/zones established.

METHODS

Enviropacific implemented a systematic approach to the remediation of the site, splitting it into four distinct zones, western, northern, eastern and central, to allow remediation to occur as per the outlined objective. Initially the central section of the site was completed to allow sufficient time for all the required council permits (demolition, hoarding, building, road opening) to be obtained and implemented. Two temporary boundary retention systems, comprising bored piles and a stabilised sand wall, were installed along two boundaries to ensure stability of the adjacent streets during remediation works. Impacted soil was excavated in accordance with the PCB pre-classification, in distinct layers/areas and either temporarily stockpiled and covered onsite and/or disposed directly to the receiving facility.

All materials, both PCB containing and PCB free materials, were tracked using a 'cradle to grave' tracking system, which allowed the precise location and/or date of disposal to be tracked for each section of the site, i.e. the unique number and location of the impacted material, the temporary stockpile number and its location and finally the EPA certificate number for each individual load.

RESULTS AND DISCUSSION

Table 1. Summary of Exported Material

	Units	Project Total
PCB impacted Perched/Storm water treated/discharged to Trade Waste	kL	47.5
PCB contaminated material transported for Thermal Treatment	tonnes	11848
PCB contaminated material transported to Landfill	tonnes	3762
PCB Free Category C material transported to Landfill	tonnes	96
PCB Free odorous Fill material transported to Landfill	tonnes	4324
PCB Free concrete transported to recycling facility	tonnes	1812
PCB impacted concrete material transported for Thermal Treatment	tonnes	414

A total of 16,024 tonnes of PCB impacted material was removed to landfill or thermal treatment, with an additional 6,232 tonnes of PCB free material disposed to landfill or concrete recycling facility. Additionally, 47.5 kL of PCB impacted perched/stormwater was treated through a temporary water treatment system to allow disposal via trade waste.

CONCLUSIONS

In December 2014 Enviropacific successfully completed soil remediation at the Site in accordance with the site specific EIP and clean-up objectives. We now have been engaged to complete the second phase of works, groundwater remediation, under a separate contract.

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POTENTIAL IMPACTS OF TILLAGE SYSTEMS ON THE MICROBIAL DYNAMICS IN SEQUESTERING CARBON

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INTRODUCTION

Agricultural management practices (such as tillage and residue management) affect the physical and chemical characteristics of the soil, which in turn influences the soil microorganisms as a function of the soil biological environment (Gonzalez-Quiñones et al. 2011; Guzman & Al-Kaisi 2010; Wardle & Ghani 1995). According to the study conducted by Chaplot et al. (2015); Guo et al. (2014) revealed that under no-till (NT) soil conditions the protection fo soil organic carbon (SOC) are more, which corresponds due to higher microbial biomass accumulation (20%) and lower CO_2 emissions (22%). Therefore, it is imperative to investigate the role of soil biogeochemical properties including different microorganisms (fungal, bacteria) which plays an important role in the formation, stabilization and degradation of soil structure to understand the SOC sequestration from a short-term (2 year) experiment.

METHODS

Soil samples were collected with the help of auger (inner diameter 50 mm) upto a depth 30 cm at three random points under no-tillage (NT) and conventional tillage (CT) systems treated with different levels of mulching (0, 2.5 and 5 t/ha). These soil samples were divided into three depths 0–100, 100–200 and 200–300 mm for basal soil respiration (BSR) and soil was incubated for three different set of period 24, 120, 288 hrs under laboratory conditions at 22 ± 1°C. Three bulk samples collected at random made into composite samples to analyse microbial biomass carbon (MBC), dehydrogenase activity (DHA) and fungal and bacterial biomass. The fungal and bacterial biomass were determined using antibiotics like cycloheximide (16mg/gm of soil) and streptomycin sulphate (14 mg/gm of soil), by trapping the CO_2 using an alkali (0.5M NaOH) solution through platting technique. The entire experiment was carried out with three replications.

RESULTS AND DISCUSSION

Our results demonstrated from the total 288 hours of incubation indicate that cumulative CO_2 emitted from the mineralizable carbon under NT from 0-10 cm depth was significantly lower ($P<0.05$) by percent decrease (22% to 39%) across mulching levels than CT system. Further, it was found that DHA and MBC were both significantly higher ($P<0.05$) under NT, namely 46%, 49.6%, 74.7% (DHA) and 28%, 34.5%, 39% (MBC) across the mulching levels (0, 2.5, 5 t/ha) respectively. In general, it was found that the DHA and MBC decreased with the increase in depth (0-10, 10-20 and 20-30 cm) with the increase in mulching rate (0, 2.5 and 5 t/ha) in both the tillage systems. However, the microbial biomass of fungal and bacterial activities were determined through platting technique method and it was found that bacterial activity were dominated by fungal activity irrespective of the tillage system, but during the first 24hrs of incubation fungal activity were higher under CT, and later it was dominated by bacterial activity under NT system. The reason of high microbial activity may be due to contact between soil and plant residues as they are closely associated with soil properties like SOC and aggregate size which essential for the development of hyphae**.**

CONCLUSIONS

In conclusion, it is expected that the relative abundance of MBC and DHA in the top layer is higher in NT than CT. An increase in fungal activity with respect to tillage may also be an important index for changes in soil qualities. However, the activity of different microorganisms (bacteria and fungi) under different tillage systems can significantly affect the C cycling and storage due to its unique structures and differential interactions with the soil physical properties.

REFERENCES

Chaplot, V, Abdalla, K, Alexis, M, Bourennane, H, Darboux, F, Dlamini, P, Everson, C, McHunu, C, Muller-Nedebock, D, Mutema, M, Quenea, K, Thenga, H & Chivenge, P 2015, 'Surface organic carbon enrichment to explain greater CO_2 emissions from short-term no-tilled soils', *Agriculture, Ecosystems & Environment,* vol. 203, pp. 110-118.

Gonzalez-Quiñones, V, Stockdale, EA, Banning, NC, Hoyle, FC, Sawada, Y, Wherrett, AD, Jones, DL & Murphy, DV 2011, 'Soil microbial biomass—Interpretation and consideration for soil monitoring', *Soil Research,* vol. 49, no. 4, pp. 287-304.

Guo, L-J, Zhang, Z-S, Wang, D-D, Li, C-F & Cao, C-G 2014, 'Effects of short-term conservation management practices on soil organic carbon fractions and microbial community composition under a rice-wheat rotation system', *Biology and fertility of soils*, pp. 1-11.

Guzman, JG & Al-Kaisi, MM 2010, 'Soil carbon dynamics and carbon budget of newly reconstructed tall-grass prairies in south central Iowa', *Journal of Environmental Quality,* vol. 39, no. 1, pp. 136-146.

Wardle, DA & Ghani, A 1995, 'A critique of the microbial metabolic quotient (qCO_2) as a bioindicator of disturbance and ecosystem development', *Soil Biology and Biochemistry,* vol. 27, no. 12, pp. 1601-1610.

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