

CleanUP 2011

4th International Contaminated Site Remediation Conference

Program and Proceedings



11 - 15 SEPTEMBER 2011

HILTON ADELAIDE HOTEL, SOUTH AUSTRALIA

4th International Contaminated Site Remediation Conference

Program and Proceedings

11-15 September 2011
Hilton Adelaide hotel



Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
September 2011

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ISBN: 978-1-921431-29-6

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These proceedings should be cited as:

CRC CARE 2011, *4th International Contaminated Site Remediation Conference: Program and Proceedings*, CleanUp 2011 Conference, Adelaide, Australia, 11–15 September 2011.

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CONFERENCE WELCOME



Dear colleagues

On behalf of CRC CARE and the Australian Remediation Industry Cluster (ARIC), it is my pleasure to welcome you to the biennial 4th International Contaminated Site Remediation Conference, being held at the Hilton Adelaide hotel, in South Australia.

With outstanding speakers from the United Kingdom, United States, Hong Kong, Taiwan, Malaysia, Italy, China, Germany and Australia, as well as delegates from more than twenty countries, this year's conference truly has an international audience.

I'm sure that delegates including scientists, engineers, regulators, and other environmental professionals will find much to stimulate and interest them in these quality presentations, and there is also plenty of time scheduled for interaction and reflection.

I would like to thank all those who made submissions for conference presentations, be they workshops, posters, papers or keynote addresses. Your commitment to sharing your expertise and knowledge is invaluable and much appreciated.

Again the conference has been very well supported by our sponsors, without whom the conference would not be possible.

Finally, I extend my thanks to the members of the organising committees who have generously given of their time and expertise to ensure CleanUp 2011 meets the needs of the various industry sectors represented by the attending delegates.

We look forward to your participation at this year's Conference in the 'City of Churches' for what I'm sure you will find a professionally rewarding and enjoyable conference experience

Professor Ravi Naidu
Managing Director, CRC CARE



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.

A structured research program is complemented by a focus on educating and training post-graduates and industry professionals, to support 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



The goal of ARIC is to create a forum for private and public organisations to consider and address macro issues that impede efficient and effective remediation of contamination, to assist with and promote communication across the industry, and to provide strategic direction for the sustainable growth of the remediation industry. ARIC also facilitates the transfer of technology and information from CRC CARE to industry and end-users.

For more information visit: www.remediationaustralasia.com

ORGANISING COMMITTEES

International organising committee

Ravi Naidu (AUS) – Coordinator and Chair (CRC CARE)
Volker Birke (Germany)
Joop Harmsen (Netherlands)
Roger Klein (UK)
Steve McGrath (UK)
Simon Pollard (UK)
Kirk Semple (UK)
Rao Surampalli (USA)
Ming Wong (Hong Kong)

Local organising committee

Ravi Naidu – Conference Chair (CRC CARE)
Andrew Beveridge (CRC CARE)
Nanthi Bolan (UniSA)
Sreenivasulu Chadalavada (CRC CARE)
Albert Juhasz (UniSA)
Bruce Kennedy (CRC CARE)
Enzo Lombi (UniSA)
Meredith Loxton (CRC CARE)
Megharaj Mallavarapu (UniSA)
Suzanne McHale (CRC CARE)
Sharmin Patard (CRC CARE)
Prashant Srivastava (CRC CARE)
Mike Williams (CRC CARE)

Plevin and Associates - Conference secretariat

4th International Contaminated Site Remediation Conference

SPONSORS

We wish to thank all sponsors for their contributions to the success of this Conference:

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Conference supporters



Short course sponsors





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E: awebber@soilandgroundwater.com.au

Melbourne

T: 03 9372 6800
F: 03 9372 6900
E: dunn@soilandgroundwater.com.au

SOCIAL PROGRAM

Welcome reception

Date: Sunday 11 September 2011

Time: 5.00pm – 5.30pm

Venue: Hilton Adelaide hotel, Gallery foyer, Level 1

The welcome reception will be held on Sunday evening prior to the official opening of the conference. This will be a great opportunity to meet colleagues before the Conference commences. The Conference will be officially opened by the Hon. Paul Caica MP, South Australian Minister for Environment and Conservation.

'Great Aussie BBQ'

Date: Monday 12 September 2011

Time: 6.00pm – 10.00pm

Venue: The Kings (formerly King's Head Hotel)

357 King William Road, Adelaide (corner King William & Sturt Streets)

Cost: \$65 per person

Enjoy the best of what South Australia has to offer your tastebuds at the 'Great Aussie BBQ' dinner on Monday evening. The barbecue will be held at The Kings, a unique South Australian-only produce bar and restaurant right in the heart of Adelaide's CBD. It's just a 5 minute walk from the conference venue, and will give you an opportunity to relax and socialize in an informal setting. Experience this much-loved Aussie tradition, which will include dishes and delicacies from South Australian regions. Tickets can be purchased from the registration desk. Note: limited spaces available.



Conference gala dinner

Date: Wednesday 14 September 2011

Time: 7.00pm – 12.00am (midnight)

Venue: Adelaide Hilton hotel ballroom

Cost: \$130 per person

The conference gala dinner will be held on Wednesday evening in the grand ballroom of the Hilton Adelaide hotel. What promises to again be a highlight of the conference the gala dinner will be a chance to recognise those keynote speakers and individuals who have made a significant contribution to the conference whilst enjoying a social gathering with colleagues and clients. With a fantastic line up of entertainment, the conference gala dinner is an event you will not want to miss.

Ticket purchase includes three course meal, drinks and entertainment, and can be purchased from the registration desk.

GENERAL INFORMATION

Registration desk opening times

Registration is located on the first floor of the Hilton hotel. Opening times are:

Sunday 11 September	8:00am – 6:00pm
Monday 12 September	7:30am – 5:00pm
Tuesday 13 September	7:30am – 5:00pm
Wednesday 14 September	7:30am – 5:00pm
Thursday 15 September	7:30am – 3:00pm

Notes to presenters

Presenters are requested to report to the registration desk. You will be directed to the speaker preparation room where your presentation will be downloaded and verified. Please meet with your session chairperson in the session room 10–15 minutes prior to the commencement of the session. The speaker preparation room will be open during the following times:

Sunday 11 September	4:00pm – 7:00pm
Monday 12 September	7:30am – 5:00pm
Tuesday 13 September	7:30am – 5:00pm
Wednesday 14 September	7:30am – 5:00pm
Thursday 15 September	7:30am – 3:00pm

If at all possible, please check-in your presentation material well before your presentation.

Special dietary requirements

If you have advised the organisers of a special dietary requirement, this information has been forwarded to the catering staff. However, it is your responsibility to identify yourself to staff.

Name tags

Name tags and lanyards are in your delegate envelope. For security reasons, and for easy recognition, please wear your name tag to each conference function.

Dress standard

Smart casual dress is suggested for conference sessions and social functions.

Messages

A message board will be set up near the registration desk – please check regularly for messages.

Mobile phones

Participants are asked to ensure that all mobile phones are switched off during conference sessions.

Smoking

The Conference has designated this to be a non-smoking environment for all sessions and social functions.

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GENERAL INFORMATION

Eating out – Restaurant suggestions (all Adelaide CBD, unless marked otherwise)

Amalfi Pizzeria

29 Frome Street / Ph: (08) 8223 1948

This much-loved Italian bistro is going strong after more than two decades of service. Amalfi has a buzzy vibe with simple menus and swift, friendly service. The wine list is full of interesting local and imported labels, plus back-vintages and hard-to-find beauties.

Auge

22 Grote Street / Ph: (08) 8410 9332 / www.auge.com.au/asp/home.aspx

Fine Italian dining; the ambience is delightful and the menu superb. Not a 'pizza and pasta' style restaurant. Winner of the 2010 'Restaurant & Catering SA Award for Excellence 2010' for 'Best Italian'. Antipasti available any time of the day.

Bistro Dom

24 Waymouth Street / Ph: (08) 8231 7000 / www.bistrodom.com.au

All day breakfasts let you sneak in a Belgian waffle before your day starts but if you stayed up past your bedtime the night before, slink in late for your egg fix. Owner Ben Johnston's philosophy is to present classic dishes with simple, fresh flavours that work in harmony.

British India

270-274 Morphett Street / Ph: (08) 8212 2411 / www.britishindia.net.au

A slightly modern take on Indian food, in stylish surroundings.

Celsius

95 Gouger Street / Ph: (08) 8231 6023 / www.celsiusrestaurant.com.au

A relatively new restaurant established by former Manse chef, Ayhan Erkoc. His team present beautiful food with a level of commitment to local produce that is highly admirable. The floor staff are friendly, efficient and knowledgeable, and nothing is too much trouble.

Chesser Cellars

29 Chesser Street / Ph: (08) 8223 3791 / www.chessercellar.com.au

Chesser Cellars is an Adelaide treasure. The meals are just right and the choice of wines by the bottle and glass is excellent. The friendly and efficient staff ensure your lunch experience is unique. Choose from their fresh seasonal menu, great coffees and daily house baked muffins.

Chianti Classico

160 Hutt Street / Ph: (08) 8232 7955 / www.chianticlassico.com.au

This family orientated restaurant continues its culinary consistency that has kept regular customers coming back for more than 20 years. It has been a consistent award winner for food and wine, and professional knowledge and service. Staff are attentive and knowledgeable; the wine list extensive and well cared for by an enthusiastic sommelier.

Chloe's

36 College Road, Kent Town / Ph: (08) 8362 2574 / www.chloes.com.au

This acclaimed restaurant is situated in a stunning 1876 Victorian villa, just a few minutes drive from the CBD. Classic dishes are created with a modern edge and served by highly experienced staff. It offers one of the country's top wine lists with a range of more than 10,000 bottles in their cellar.

Concubine

132 Gouger Street / Ph: (08) 8212 8288 / www.concubine.com.au

Winner of awards for Best Chinese restaurant for the past two years. A refined take on Chinese cuisine, and located next door to a sangria bar for later in the evening.

GENERAL INFORMATION

Gaicho's

91 Gouger Street / Ph: (08) 8231 2299 / www.gauchos.com.au

A huge range and variety of mainly meat dishes (and some fish), specialising in authentic Argentinean cuisine. The mixed grill platter may have been modelled on Noah's Ark. Believed to have the biggest and best steaks in Adelaide. Order a T-Bone and you will have to choose 750g or 1kg! Winner of numerous 'Awards for Excellence'. Their chimichurri has to be tasted to be believed.

Jam the Bistro

112 Wright Street / Ph: (08) 8231 7411 / www.jamthebistro.com.au

This funky contemporary bistro lets diners peek into the genuinely smart, modern kitchen to watch the chefs concoct their magic. Since bursting onto the city dining scene in early 2009, Jam has already become a favourite for pick-me-up breakfast starts, stunning lunches, and intimate dinners. It delivers Mediterranean favourites in a fresh and energetic style.

La Trattoria

346 King William Street / Ph: (08) 8212 3327 / www.latrattoria.com.au

Situated around the corner from the court on King William Street, and run by the Parisi family for as long as anyone can remember. Popular for those who enjoy pizza, pasta, scallopine and parmigiana style of Italian food, in a rustic setting.

Magill Estate

78 Penfold Road, Magill / Ph: (08) 8301 5551 / www.penfolds.com.au/brand_penfolds/index.htm

Nestled in the foothills of Adelaide and only 15 minutes drive from the CBD, the historic Penfolds Magill Estate is the original home of Penfolds wines and of Australia's most prized wine, the famous Grange. A contemporary dining venue offering modern Australian dishes, overlooking the shiraz vines and the city of Adelaide.

Mesa Lunga

140 Gouger Street / Ph: (08) 8410 7617 / www.mesalunga.com

The only place in Adelaide worthy of calling itself a tapas specialist, whilst also serving Spanish favourites such as their classic paella. Enjoy the comfortable and sociable atmosphere with a jug of sparkling sangria.

Paul's

79 Gouger Street / Ph: (08) 8231 9778

Paul's has been serving top quality fish for more than 60 years with fresh King George whiting, barramundi, oysters, prawns and Moreton Bay bugs all on the menu. There are a number of other fish restaurants in Gouger Street serving good quality seafood, including **Stanley's** (76 Gouger Street / Ph: (08) 8410 0909).

Rigoni's

27 Leigh Street / Ph: (08) 8301 5551 / www.rigonis.com.au

Since 1979, Rigoni's has been the lunch haunt for South Australian business people and politicians serving up the best of Italian food in a relaxed bistro atmosphere, with great service and superb wines. Situated in the historic and beautifully restored Leigh Street; a short stroll from the city's major hotels and equally convenient to Adelaide's central business district, theatre precinct and central markets. Winner Best Breakfast 2010 National Awards, and SA.

Star House

31 Gouger Street / Ph: (08) 8221 6303

Good yum cha and good value.

Star of Siam

67 Gouger Street / Ph: (08) 8231 3527 / www.starofsiam-adelaide.com.au

One of the most popular Thai restaurants in Adelaide and particularly popular with the legal profession during the day. Founded in 1987 by two sisters, Somchit and Valeerat, Star of Siam has been awarded numerous accolades over the last 23 years and has great staff that will look after you. Well priced.

GENERAL INFORMATION

Other facilities

Banks

Commonwealth Bank	100 King William Street
Bank SA	97 King William Street
ANZ	121 King William Street
National Bank	22 – 28 King William Street
Westpac	2 – 8 King William Street

Post office

GPO 141 King William Street

Pharmacies

Midnight Pharmacy	13 West Terrace, Adelaide (08) 8231 6333
National Pharmacy	52 Gawler Place, Adelaide (08) 8223 6373

Public transport

Adelaide Metro Infoline	
Bus, train & tram timetables	Corner King William and Currie Streets 1300 311 108 / www.adelaidemetro.com.au

Taxis

Adelaide Independent Taxi	13 22 11
Suburban Taxi	13 10 08
Yellow Cabs	13 22 27

Car parking

There are public car parks near the Hilton Adelaide hotel, including:

U Park	21 – 59 Grote Street (<i>above Central Market</i>)
	Monday to Thursday 7:00am – 12:00am (midnight)
	Friday & Saturday 6.30am – 1:00am
	Sunday 9:00am – 10:00pm
	Weekday charges over 6 hours, \$26.50

U Park	82 Grote Street (<i>Adelaide Bus Station</i>)
	Monday to Saturday 6.30am – 12:00am (midnight)
	Sunday 10:00am – 10:00pm
	Weekday charges over 6 hours, \$26.50

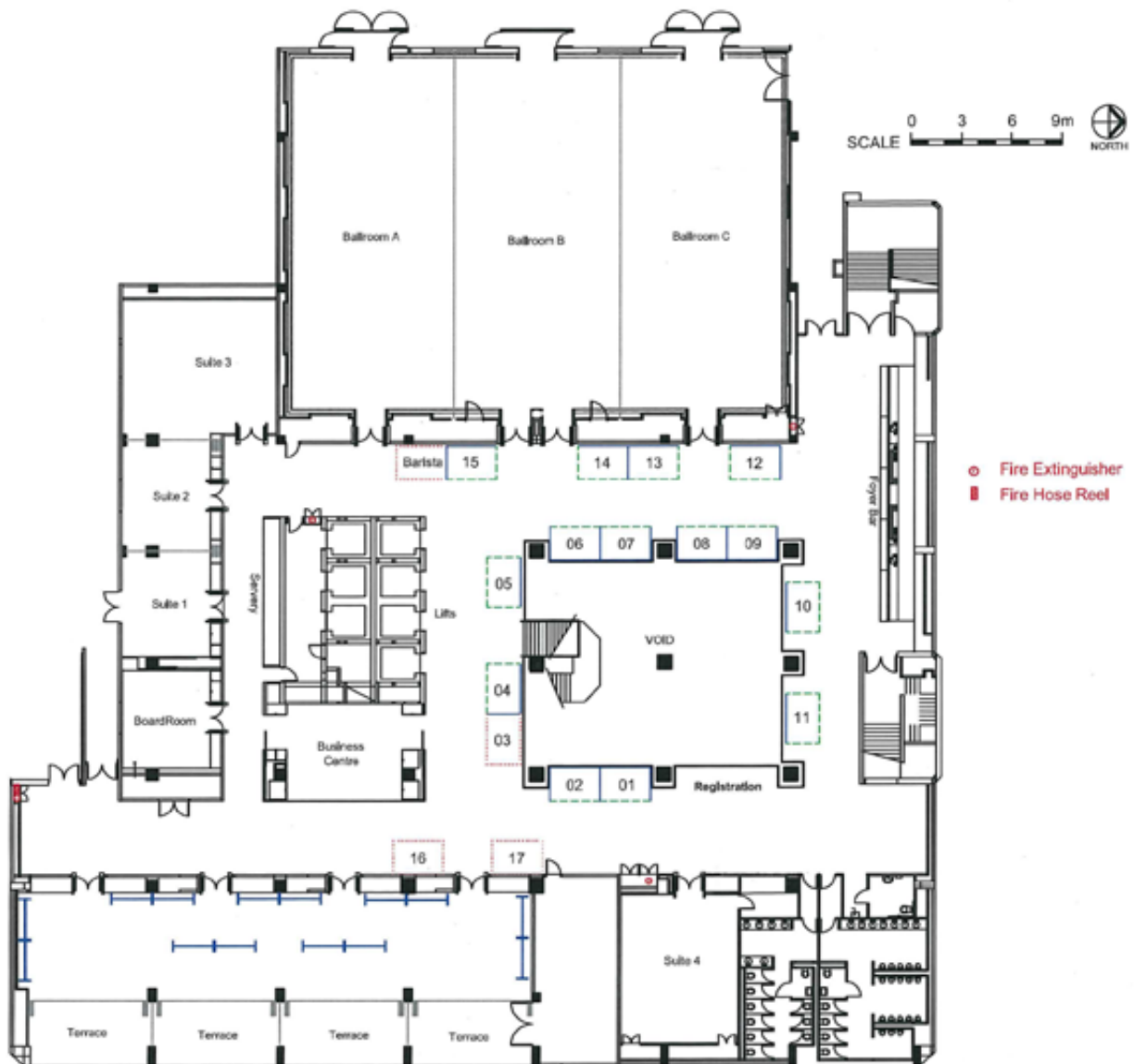
EziPark	102 Wakefield Street (<i>entry via Roper Street</i>)
	Monday to Thursday 6:00am – 9:00pm
	Friday & Saturday 6:00am – 12:00am (midnight)
	Sunday 10:00am – 9:00pm
	Weekday charges over 3 hours, \$23

Medical and emergency services

For emergencies requiring ambulance, fire or police attendance, dial 000. This applies in every state of Australia. Medical services are not provided free to visitors.

For incidents requiring police attendance call	13 14 44
Poisons Information Centre call	13 11 26
Lifeline Counselling Service call	13 11 14

EXHIBITORS



Exhibitor locations

Booth 1 & 2	CRC CARE	Booth 10	Shell
Booth 3	ERR	Booth 12	FMG Engineering
Booth 4	Airwell Pumps Pty. Ltd.	Booth 13	SGS
Booth 5	Ziltek Pty. Ltd.	Booth 14	Thiess Services
Booth 6	Dynapumps	Booth 15	ALS Environmental
Booth 7	Enviropacific	Booth 16	FMC Corporation
Booth 8	Hydro Terra	Booth 17	Thermo Fisher Scientific
Booth 9	CheckSite		

EXHIBITORS

Trade exhibition

The Conference Organising Committee thanks exhibitors for their support.

Exhibition opening times

The trade exhibition is located in the Hilton Adelaide hotel, and will be open during the following hours:

Sunday 11 September	6:00pm – 8:00pm
Monday 12 September	9:00am – 5:00pm
Tuesday 13 September	9:00am – 5:00pm
Wednesday 14 September	9:00am – 5:00pm
Thursday 15 September	9:00am – 5:00pm

CRC CARE (Booths 1 and 2)

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. A structured research program is complemented by a focus on educating and training post-graduates and industry professionals to support the growth of highly qualified and suitably trained researchers and decision-makers in the area of environmental risk assessment and remediation.

ERR (Booth 3)

Environmental Remediation Resources (ERR) supplies a range of resources for site investigation and remediation. Our customised approach and competitive offering includes sampling equipment, passive soil gas surveys, microbiological diagnostics, groundwater mapping, pneumatic pumps, skimmers, vapour treatment, air strippers, filtration vessels and media, bioremediation, surfactants, chemical oxidation/reduction, system design and installation.

Airwell Pumps Pty Ltd (Booth 4)

Airwell Pumps specialise in the manufacture, supply and installation of low flow rate, remote from power, corrosive resistant, self-regulating and intrinsically safe pumping systems for leachate/pollution recovery, groundwater remediation, salinity management and water sampling. Airwell pumps have been used in some of the largest contaminated site remediation projects in Australia.

Ziltek Pty Ltd (Booth 5)

Ziltek is a leading provider of waste remediation products and services. The company provides turnkey solutions for hazardous waste treatment including optimisation trials, regulatory approvals and the supply of treatment products. In 2011, Ziltek launched a new hire service for the rapid in-situ measurement of petroleum hydrocarbons – a skilled operator takes measurements using a hand-held device with the patented RemScan™ method on board. The company also markets a range of products for chemical fixation (RemBind® F), bioremediation (RemActiv™) and odour control (RemBind® O).

Dynapumps (Booth 6)

Dynapumps is exhibiting low carbon and contaminant free products including the new Blackhawk Apollo, solar powered piston pumps with motors above the wellhead used for landfill leachate and groundwater remediation and Dynapumps oil, and water-free, rotary claw vacuum and blower packaged systems for methane gas removal and regeneration.

Enviropacific (Booth 7)

Enviropacific Services are industry leaders in site remediation and industrial waste management, including the treatment of contaminated soils, water and by-products from industry. We have extensive expertise in delivering efficient and cost effective environmental remediation solutions to a broad range of public sectors and private enterprise. Our success is a result of the way we conduct our business. We place the highest importance on client satisfaction, cost effective project delivery, QHSE and compliance with relevant laws and regulations. Our high level of repeat business demonstrates this commitment.

Hydra Terra (Booth 8)

HydroTerra offers a full scope of the most advanced technologies worldwide for testing and monitoring the environmental parameters of water, soil and air. HydroTerra's services include sales, rental, and project work. Their team of scientists, engineers and hydrogeologists are available to offer technical advice and solutions.

EXHIBITORS

CheckSite (Booth 9)

CheckSite is a one-stop-shop for environmental auditors supplying authoritative, land-specific information including site, environmental, historical and geology and groundwater reports.

Shell (Booth 10)

Shell's internationally-recognised environmental experts leverage partnerships with academic, regulatory, consulting and industry stakeholders to provide technically sound solutions in response to contaminated soil and groundwater challenges. From a unique perspective as an owner/operator, Shell develops practical and sustainable risk-based solutions to protect human health and the environment.

FMG Engineering (Booth 12)

Founded in South Australia, FMG Engineering grew from Koukourou Engineers and has provided a wide range of services to clients in South Australia since 1972. FMG Engineering has its head office in Adelaide, and another office in Melbourne. Services include civil engineering through to environmental services and structural engineering. Twelve experienced environmental practitioners offer specialist advice in areas such as contaminated land and groundwater management, hazardous waste and due diligence.

SGS (Booth 13)

In Australia, SGS operates in a network of over 60 offices and laboratories with head office in Perth and major facilities in Sydney, Melbourne, Adelaide and Brisbane. Recognised as the benchmark for quality and integrity, SGS employs more than 59,000 people globally, and operates a network of more than 1,000 offices and laboratories around the world. Within SGS, best practice is dominant in all areas of business and is encouraged at all times, whether working internally within the SGS Group, servicing customers, or simply being good corporate citizens. Best practice to SGS is more than a good business decision – it is a part of, and firmly entrenched in, our culture.

Thiess Services (Booth 14)

Thiess Services is Australia's oldest, largest and most experienced contractor. We pioneered many of the remediation practices that are used today, and we are still innovating. We have completed over \$1 billion of remediation project works, and have 25 years of experience in oil, gas, chemical, radiological mining and sediment remediation.

ALS Environmental (Booth 15)

ALS is a diversified global testing organisation, with a solid commitment to client services, R&D, quality and NATA accreditation. The Environmental Division provides high quality and dependable analytical testing data to assist consulting and engineering firms, industry, and government agencies around the world in making informed decisions for environmental projects.

FMC Corporation (Booth 16)

FMC is a diversified chemical company that has been serving industrial and consumer markets for over a century. A leader in chemical oxidation for environmental applications, FMC offers Klozur® activated persulfate, PermeOx® Plus, and hydrogen peroxide for remediating a wide range of contaminants including petroleum hydrocarbons, BTEX, chlorinated solvents, MTBE and pesticides.

Thermo Fisher Scientific (Booth 17)

Thermo Fisher Scientific delivers a range of specialised technology-focussed monitoring, analysis and treatment products, instrument servicing and professional application support into the environmental market. They offer systems for landfill, water, wastewater, groundwater, sludge dewatering and site remediation; well drilling materials and equipment; plus a nationwide rentals service across all fields.

PLENARY AND KEYNOTE SPEAKERS

Plenary speakers



Mr Dennis Monahan

Mr Dennis Monahan is a specialist in regulatory environmental management with over 30 years experience in this area. His graduate qualifications are in chemical engineering, and town and regional planning, with postgraduate qualifications in environmental engineering. He has a strong background in all aspects of EPA operations including policy and legislation development, assessment and licensing, monitoring, enforcement, and emergency response. His specific areas of technical expertise are in hazardous waste, contaminated land, and water quality issues. With respect to contaminated land, he was at the forefront of the development and implementation of approaches to clean up and manage contaminated land in Victoria in the late 1980's and early 1990's. This included establishing and overseeing the first environmental audit system in Australia, providing resources and directing EPA Victoria input to developing the first National Environment Protection Measure, developing and applying legislative approaches such as clean up notices, and managing site clean ups undertaken by EPA Victoria. Mr Monahan worked closely on the above, and other environmental management issues, with former EPA Victoria Chair Dr Brian Robinson over many years. His final position at EPA Victoria was as Director Environmental Sciences, where he continued to have corporate responsibility for strategic approaches to contaminated sites issues as well as responsibility for its monitoring, laboratory and scientific studies across land, water, and air environments. Since leaving EPA in 2005, Mr Monahan has maintained a strong interest in a number of environmental areas, and continues to provide advice to EPA Victoria on regulatory matters. He has also chaired the CRC CARE Project Advisory Group consisting of industry, regulator, and research representatives overseeing the delivery of key projects related to hydrocarbon contamination.



Associate Prof. Brajesh Singh, University of Western Sydney, Australia

Dr Singh is an Associate Professor at the Hawkesbury Institute for the Environment, University of Western Sydney. He is a toxicologist and ecologist with expertise in chemistry, genomics, microbiology and ecological risk assessment (ERA). Since 2002, he has appeared in more than 100 publications and given presentations in the areas of the biodegradation/bioremediation, eco-toxicology, and microbial ecology. His current research projects include development of technologies for effective biodegradation/bioremediation of heavy metals and anthropogenic (agrochemical and industrial) pollutants. In recent years, Dr Singh has explored the impact of climate change on the environment including pollutant degradation. Over the past five years, he has been frequently invited by various international conferences/workshops to give talks and chair sessions. Dr Singh is currently a senior editor for the journal *Biodegradation* (Springer publication), and serves as an editorial board member for *Environmental Toxicology and Chemistry* (Wiley-Blackwell), *Applied and Environmental Microbiology* (American Society of Microbiology) and *Scientific Reports* (Nature Publication). He has been an elected member for several academic societies and funding bodies, including the SETAC-UK Council and Board of Directors (2004–2011) and the Peer College Review Member for National Environmental Research Council (2007–2011), UK.

PLENARY AND KEYNOTE SPEAKERS

Invited keynote presenters

Prof. Renato Baciocchi, University of Rome

Professor Baciocchi is Assistant Professor of Environmental Engineering at the University of Rome Tor Vergata since 2003. He received a Ph.D. in Chemical Engineering by the Politecnico di Milano in 1995, and worked for a few years as process engineer before starting his academic career at the end of 1998. His main research interests focus on remediation of contaminated sites and carbon dioxide capture and storage. In the former field, he has been working on the application of in-situ chemical oxidation (ISCO) to the remediation of contaminated sites and on the development of tools and criteria for the application of risk analysis to the management of contaminated sites. He is currently a member of a working group of the Ministry of The Environment on the issue of the national priority contaminated sites. He has published more than 100 contributions to international journals and conference proceedings, with 39 papers published in peer reviewed journals.



Dr Volker Birke, Ostfalia University, Germany

Dr Birke has over 20 years of experience in organic and environmental chemistry, particularly in green chemistry and the destruction of hazardous wastes and toxic compounds in the environment. He has experience in remediation of contaminated sites, hazardous waste management, and groundwater remediation, and has also acted as the coordinator of the large-scale German R&D cluster RUBIN for the application of permeable reactive barriers (PRBs).



Dr Greg Davis, CSIRO Land and Water

Dr Davis is leading multidisciplinary research on groundwater quality science and urban water environment research with CSIRO. Dr Davis joined CSIRO's Division of Groundwater Research in 1983, after completing his doctoral studies on the topic of pyritic oxidation in mining industry waste rock dumps at the University of Wollongong, New South Wales, Australia, and the then Australian Atomic Energy Commission (now ANSTO). He now leads a multidisciplinary group that also generates research supporting resource and energy sector industries, such as innovative approaches to mineral and petroleum recovery, reuse of mineral industry wastes, and geothermal energy. Research topics of special interest have included: the behaviour and fate of chemicals in subsurface environments, including organics (e.g. petroleum hydrocarbons, solvents, pesticides, munition compounds, trace organics), nutrients (e.g. nitrate, ammonium) and metals; chemical fluxes in groundwater, and especially fluxes to marine and estuarine environments; quantifying vapour biodegradation and risks; and evaluating remediation and treatment technologies at field scale.



Dr Jamal Hisham Hashim, International Institute for Global Health, United Nations University

Dr Hashim is a research fellow and a professor of environmental health at the International Institute for Global Health, United Nations University (UNU). He was formerly a professor at Universiti Kebangsaan Malaysia (UKM). He obtained his undergraduate degree in biology and environmental studies, and his Masters and PhD in environmental health from 3 universities in the U.S. He has been teaching, conducting research and consultancy in environmental and occupational health at UKM and UNU for the past 29 years. His research interests are mainly on the health effects of heavy metals, pesticides, solvents, air pollution, and recently, climate change. He has been the principal investigator of 9 research projects and co-investigator of another 5 projects, and has over 230 publications and presentations to date. Dr Jamal has been engaged as an environmental health consultant in over 50 local and overseas projects, primarily in the area of environmental health impact and risk assessment. He has also been consulted by the World Health Organization, Risk Science Institute in the U.S., and the governments of Malaysia, Cambodia, Indonesia and Saudi Arabia on various environmental health issues. He is a registered environmental impact assessment consultant with the Department of Environment, Malaysia, and a member of the Chartered Institute of Environmental Health in the UK.



Prof. Jimmy Kao, National Sun Yat-Sen University, Taiwan

Professor Kao holds a Bachelor degree in Environmental Engineering, and a Masters and Ph.D. in Civil Engineering. He is currently the Professor and Director of the Water Resource Research Centre, National Sun Yat-Sen University, Taiwan. He is a Fellow of the American Society of Civil Engineers and American Association for the Advancement of Science, and a Diplomate of the American Academy of Environmental Engineers and American Academy of Water Resources Engineers. He is also the Associate Editor of the ASCE journal, *Journal of Hazardous, Toxic and Radioactive Waste* (US) and WEF journal, *Water Environment Research* (US), and an editorial board member for the *Taiwan Soil and Groundwater Environmental Bulletin* (Taiwan) and *Journal of Environmental Engineering and Management* (Taiwan).



PLENARY AND KEYNOTE SPEAKERS



Prof. Irene Lo, Hong Kong University of Science and Technology, Hong Kong

Professor Lo is currently Professor in the Department of Civil and Environmental Engineering, and Director of Environmental Engineering Program at the Hong Kong University of Science and Technology (HKUST). She is a Fellow of the Hong Kong Institution of Engineers (HKIE) and a Fellow of the American Society of Civil Engineers (ASCE). She received both her M.S. and Ph.D. from the University of Texas at Austin, USA. She is also an associate editor of the *Journal of Hazardous, Toxic and Radioactive Waste*. Professor Lo has edited 4 books and published more than 250 journal and conference papers in the areas of remediation technologies for contaminated soils and groundwater, magnetic nano- and microparticles for environmental pollution control, carbon footprint analysis and life cycle assessment of remediation technology, waste containment facilities, and pollutant migration in soils.



Dr Frank Lamé, Deltares, Netherlands

Dr Lamé works for the Netherlands research organisation 'Deltares', which specialises in the sustainable development of delta areas: Enabling Delta Life. Deltares is the key knowledge institute for the Dutch Ministry of Infrastructure and Environment. Currently, Frank coordinates all activities within the yearly research program for the Ministry. Dr Lamé started his professional carrier in the environment in 1985 with the Netherlands Organisation for Applied Scientific Research TNO, for which he was employed until 2009. His primary area of expertise lays in soil contamination and soil remediation, with a specific focus on soil protection and the development of testing and assessment methods for soils, (secondary) building materials and waste. As such, he has been directly involved in the development of the soil policy in the Netherlands over a period of approximately 15 years. Since 2001, Dr Lamé is the Chairman of the Technical Standardisation Committee ISO/TC 190 'Soil Quality', and since 2003 he is also Chairman of the European Standardisation Committee CEN/TC 345 'Characterisation of Soils'.



Prof. Lena Ma, University of Florida, USA

Professor Ma received her M.S and Ph.D degree from Colorado State University in environmental soil chemistry. She is currently a Professor in the Soil and Water Science Department at University of Florida, USA. For the past 25 years, she has been working in the areas of biogeochemistry of trace metals in soil-water-plant-microbe ecosystems, and phytoremediation and chemical remediation of trace metal-contaminated water, soils, and wastes. She is a Fellow of American Society of Soil Science and the American Society of Agronomy. She received the Discovery 2001 Award from the Royal Geographical Society and Discovery Networks Europe, and she was a recipient of USDA Secretary's Honor Award in 2004. Professor Ma has published more than 170 refereed journal articles and book chapters.



Prof. Steve McGrath, Rothamsted Research, UK

Professor McGrath is an internationally recognised authority on the chemical forms of pollutants in soils, their uptake and fate in plants and their effects on soil microorganisms. Currently he is Program Leader of Soil Protection and Bioremediation Research, and Deputy Head of the Soil Science Department at Rothamsted Research in the UK. Since 2001 he has held the position of Special Professor in the School of Biosciences in Nottingham University. He is a partner in many international research programs including those of the EU, UNEP and FAO, and is currently Secretary of the International Society for Trace Element Biogeochemistry.



Prof. Paul Nathanail, University of Nottingham, UK

Professor Nathanail is Professor of Engineering Geology at the University of Nottingham, and managing director of specialist contaminated land consultants Land Quality Management Ltd. His interest in sustainable remediation stems from a long track record in the broader field of sustainable urban land management. The concept is 'trending' and in danger of losing its impact through misuse on company websites and marketing literature. The plethora of spreadsheets, programs and applets purporting to diagnose sustainable remediation are in danger of cloaking a simple concept with overly elaborate, time consuming and expensive procedures. The middle ground in achieving a step change in how we remediate is to use simple tools and approaches to help identify those remedies likely to deliver optimal net social, economic and environmental benefits.

PLENARY AND KEYNOTE SPEAKERS

Dr Sophie Rocks, Cranfield University

Dr Rocks is a toxicologist with a background in materials science. Her particular interest is in the toxicity and risk associated with emerging technologies, specifically nanomaterials. Her current research portfolio also includes risk assessment and management, free radical chemistry and environmental impacts of nanomaterials. She is Centre Manager for the Risk Centre, leading a team of 5 research staff and 5 research students, which provide leading research on strategic risk assessment, risk and evidence, and organisational maturity within Government and organisations. Sophie helped to establish the Collaborative Centre of Excellence for Managing and Understanding Natural and Environmental Risks (Risk Centre, PI Professor Simon Pollard) in December 2008 as part of a strategic partnership between Department of Environment, Food and Rural Affairs (Defra, UK), Engineering and Physical Sciences Research Council (EPSRC), Natural Environment Research Council (NERC), and Economic and Social Research Council (ESRC). Sophie was appointed as a member of the Advisory Committee on Hazardous Substances (ACHS, UK) in September 2008.



Prof. Kenneth Sajwan, Savannah State University

Professor Sajwan is currently Professor and Director of the Environmental Science Program, and serves as the Interim Dean of Graduate Studies at Savannah State University, Savannah, Georgia, USA. He is a Fellow of the American Society of Agronomy and Fellow of the Soil Science Society of America. He received his M.S. in Public Health from Armstrong Atlantic State University and Ph.D. in Agronomy and Environmental Quality from Colorado State University, USA. He is also an Associate Editor of the *Journal of Environmental Quality* and the *Journal of Environmental Monitoring and Restoration*. Professor Sajwan has edited 5 books and two laboratory manuals, and published more than 200 journal and conference papers in the areas of biogeochemistry of trace elements, waste management, dioxins, pesticides, PPCPs, PCBs, PFCs, and PBDEs. He has also received numerous national and international awards for his teaching and research excellence. He is the recipient of the Distinguished Teacher Award of the National Science Teachers' Association; the Ernest L. Boyer International award for Teaching, Learning, and Technology; the Regents' Distinguished Professor Award; the White House Millennium Award for Teaching and Research Excellence; and the U.S. Presidential Award for Excellence in Science, Mathematics, and Engineering Mentoring.



Prof. Rao Surampalli, US EPA, USA

Professor Surampalli received his MS and PhD degrees in Environmental Engineering from Oklahoma State University and Iowa State University, respectively. He is a Registered Professional Engineer in the branches of Civil and Environmental Engineering, and also a Board Certified Environmental Engineer (BCEE) of the American Academy of Environmental Engineers (AAEE) and Diplomate of the American Academy of Water Resources Engineers (DWRE). He has authored more than 500 technical publications, including 12 patents, 11 books, 77 book chapters, 203 refereed (peer-reviewed) journal articles, presented at more than 200 national and international conferences, edited 13 refereed conference proceedings, and given over 80 plenary, keynote or invited presentations worldwide. Professor Surampalli is a Distinguished Member of American Society Civil Engineers, Fellow of the American Association for the Advancement of Science, and a Member of the European Academy of Sciences and Arts. He also is Vice-Chair of Editorial Board of *Water Environment Research Journal* and Editor of ASCE's *Journal of Hazardous, Toxic and Radioactive Waste*.



Prof. J. Keith Syers, Naresuan University, Phitsanulok, Thailand

Professor Syers was Foundation Professor of Soil Science at Massey University between 1972 and 1985. He was appointed Professor and Head of Soil Science in the School of Agriculture at Newcastle University, UK, on 1 January 1986. He was later appointed Dean of the Faculty of Agriculture and Biological Sciences from August 1991 to July 1992. He retired from the University in December 1999, at which time the title of Emeritus Professor was conferred. In 1992, he was elected Fellow of the Soil Science Society of America, and was particularly proud that three PhD students from the old Soil Science Department have also received the same award – Andy Sharpley (in 1991), Brent Clothier (in 1992), and Ravi Naidu (in 2000). His work has received widespread recognition, including Fellowship of the Royal Society of New Zealand (1981) and Fellow of the New Zealand Soil Science Society (1996), for which he was President between 1978 and 1982. In 2006, Professor Syers was awarded the International Soil Science Award for contributions to global soil science. As at 2006, he was Professor of Natural Resources, Director of the Centre for Natural Resources and Environmental Management, and Dean of the School of Science at Mae Fah Luang University in Chiang Rai, northern Thailand. Professor Syers contributed to many books, including *Agriculture and the Nitrogen Cycle: Assessing the Impacts of Fertilizer Use on Food Production and the Environment* as editor. Until 2011, he was Vice-President for International Relations at Naresuan University, Phitsanulok, Thailand. Professor Syers passed away on 16 July 2011. His presentation at the conference will be presented by his former students, Professor Nanthi Bolan and Professor Ravi Naidu.



PLENARY AND KEYNOTE SPEAKERS



Prof. Ming Hung Wong, Hong Kong Baptist University, Hong Kong

In his role as Chair Professor of Biology, Director of Croucher Institute for Environmental Sciences, HK Baptist University, Professor Wong has established a multi-disciplinary team including environmental toxicologists, molecular biologists, analytical chemists, mathematicians, medical professionals and environmental managers for tackling environmental problems. He is recognised internationally for his work on environmental impact assessment, and in particular, contaminant impact on environment health.



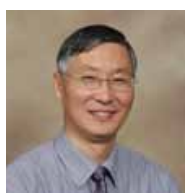
Prof. Tze Wai (TW) Wong, the Chinese University of Hong Kong

Professor Wong is currently Professor in the School of Public Health and Primary Care of the Chinese University of Hong Kong. He studied medicine in Hong Kong and then received specialist training in Public Health in Singapore. He is a specialist in Community Medicine with over 30 years of work experience in Public Health, Occupational and Environmental Health. Starting his profession as a community physician in Hong Kong, he later became an academic, first in the National University of Singapore and later, the Chinese University of Hong Kong. He has over two decades of research, teaching and consultancy experience, having served on many advisory bodies in public health, environmental health and occupational medicine in both cities. His areas of expertise include environmental health – air pollution and health, persistent organic pollutants, risk assessment, and infectious diseases. His research topics include a wide spectrum – dioxins and other organic pollutants, plague, hantaviruses, SARS, noise-induced hearing loss, environmental noise, traffic and worksite accidents, silicosis, disease mapping, cancer epidemiology, and the health of displaced populations. He has published over 170 scientific papers in peer-reviewed journals, over 110 conference papers, several books and over 30 research monographs.



Dr Eddy Zeng, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China

Dr Zeng received his B.S. degree from the University of Science and Technology of China in 1982, M.S. from Sun Yat-sen University in 1985, and Ph.D. from the University of Southern California in 1992. Dr Zeng was a principal scientist with the Southern California Coastal Water Research Project (Costa Mesa, California, USA) before relocating in China in 2004. He is currently a professor with the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and also serves as an editor of *Environmental Toxicology and Chemistry*, an associate editor of *Journal of Hydrology*, an editorial advisory board member of *Environmental Science & Technology* and *Chemosphere*. He has been conducting research in the field of environmental geochemistry, focusing mainly on the environmental occurrence and fate of persistent organic pollutants. He has authored more than 100 peer-reviewed scientific articles and several book chapters and has given invited seminars numerous times worldwide.



Dr Tian Zhang, University of Nebraska-Lincoln, USA

Dr Zhang is a Professor in the department of Civil Engineering at the University of Nebraska-Lincoln, USA. He holds a Ph.D. in environmental engineering from the University of Cincinnati. Professor Zhang specialises in water and wastewater treatment, biological wastes treatment, senior design and remediation of hazardous wastes. His research involves water, wastewater, and stormwater treatment and management, application of nanotechnologies, remediation of contaminated environments, and detection and control of emerging contaminants in aquatic environments. Professor Zhang is a member of the American Association for the Advancement of Science, American Society of Civil Engineers, the Water Environmental Federation and the Association of Environmental Engineering and Science Professors.

PLENARY AND KEYNOTE SPEAKERS

The commemorative Brian Robinson Lecture

Dr Brian Robinson AM devoted his working life to improving Victoria's environment, and shaping the direction of environmental protection in Australia.

Born in northern Ireland, Dr Robinson first came to Australia in 1968 to complete his PhD in Chemistry at Melbourne University. After a period as a research chemist with DuPont in the UK, he returned to Australia in 1973 to play a key role in the Westernport Bay Environmental study. It was here, working on one of the largest environmental studies of its type, that he consolidated his passion for the environment and his lifelong commitment to shaping a sustainable Victoria.

Brian joined EPA Victoria in 1975, and was appointed Chairman in 1986. It was he, more than anyone else, who made EPA Victoria the nation's leading environment protection agency. For more than 30 years he strived to ensure resource efficiency and sustainable goods and services. Over the last decade, his interests spread to identifying financial drivers for environmental improvements and to ways of fully engaging local communities in sustainability issues.

Recognised nationally and internationally as one of the strongest and most articulate advocates for cleaner production, Dr Robinson realised very early in his career that a robust high quality environment was central to the prosperity of society and individual enterprise.

Guided by his commitment to serving the people, Dr Robinson remains the longest serving Chairman/CEO of EPA, and is remembered as a humane and visionary leader with outstanding scientific and management skills. Brian dedicated his professional life to the improvement of environmental quality, and to ensuring that all those with a stake in environment had access to reliable, relevant information about their environment, as well as the opportunity to participate in decisions about its protection.

Sadly, Brian Robinson passed away on 1 May 2004. A valedictory celebration of his achievements was held in the Great Hall of the National Gallery of Victoria, attended by 1200 people. Politicians of all persuasions sang his praises. Bureaucrats and captains of industry spoke of his capabilities. All were unanimous in their appreciation of his ability and his charm. His sheer niceness, it seems, oiled the machinery he constructed to reconcile differing interests. He worked what miracles he could for the environment, and for people's quality of life. Brian's voice was loud and his passion was clear.

As part of the 4th International Contaminated Site Remediation Conference, the organising committee wishes to acknowledge the efforts of the late Dr Brian Robinson whose vision, ideas and leadership were recognised as a force for global sustainability, with the commemorative Brian Robinson Lecture. This year, the organising committee has extended an invitation to Mr Dennis Monahan, former Director Environmental Sciences with EPA Victoria, to present the commemorative Brian Robinson Lecture.

PROGRAM TIMETABLES

Conference program planner

		Ballroom A	Ballroom B		
Sunday 11 September	8.30 - 10.00	Workshop: Characterisation and evaluation of vapour intrusion	Workshop: Health risk assessment of contaminated sites – pitfalls and some handy tips		
	10.30 - 12.30				
	1.30 - 3.00				
	3.30 - 5.00				
	5.00 - 5.30			Welcome reception	
	5.30 - 5.45			Official opening of the 4th International Contaminated Site Remediation Conference	
	5.45 - 6.45			The commemorative Brian Robinson Lecture	
Monday 12 September	8.30 - 10.10	Permeable reactive barriers	Socio-economic drivers for remediation		
	10.40 - 12.20		Emerging contaminants		
	1.20 - 3.00				
	3.40 - 5.00				
	5.00 - 6.00			Drinks and poster session	
	6.30 - 10.00		BBQ dinner		
Tuesday 13 September	9.00 - 10.00	Plenary lecture			
	10.40 - 12.20	E-waste	Sustainable remediation		
	1.20 - 3.00				
	3.40 - 5.00			Remediation of metals and metalloids in soils and groundwater	
	5.00 - 6.00	Drinks and poster session			
Wednesday 14 September	8.30 - 10.10	BHP Billiton - Hunter River remediation project	Resource utilisation		
	10.40 - 12.40		Resource management		
	1.40 - 3.00	Remediation case studies	Resources characterisation		
	3.40 - 5.00		Resource value-addition		
	5.00 - 6.00		Drinks and poster session		
	7.00 - 12.00	Conference gala dinner			
Thursday 15 September	9.00 - 10.20	Nanotechnology for environmental remediation	Vapor intrusion: Sampling and assessment		
	10.50 - 12.30	Micro and Nanotechnology for environmental remediation			
	1.30 - 3.10				
	3.40 - 4.30	Closing plenary lecture			
	4.30 - 4.40	Conference Closing			
Friday 16 September	8.30 - 5.30	Technical Tour 1: Sustainable resource management	Technical Tour 2: Remediation technologies for contaminated soil and groundwater		

PROGRAM TIMETABLES

Conference program planner

Ballroom C	Suite 3	Balcony Room 4
Workshop: Science communication	Workshop: 1st National Forum and Workshop on fire-fighting foams and the environment	Workshop: Software solutions in groundwater – introducing MIKE SHE and FEFLOW
Workshop: Grant writing		
Welcome reception		
Official opening of the 4th International Contaminated Site Remediation Conference		
The commemorative Brian Robinson Lecture		
Innovative site assessment tools and techniques	Industry Summit	
Innovative site characterisation and assessment		
Drinks and poster session		
BBQ dinner		
Plenary lecture		
Toxicological measurements and characterisation	Regulator Session	
The effects of contaminants on human health		
Drinks and poster session		
Defence Symposium	Bioavailability of contaminants	
	Bioremediation	
	In-situ chemical oxidation	
Drinks and poster session		
Conference gala dinner		
Risk based management and cleanup approaches	Advances in chemical remediation	
	Advances in remediation technology	
Closing plenary lecture		
Conference Closing		

PROGRAM TIMETABLES

Program Sunday 11 September

	Ballroom A		Ballroom B	
8.30 - 10.00		Workshop: Characterisation and evaluation of vapour intrusion		Workshop: Health risk assessment of contaminated sites – pitfalls and some handy tips
10.00 - 10.30	Morning tea			
10.30 - 12.30		Workshop: Characterisation and evaluation of vapour intrusion		Workshop: Health risk assessment of contaminated sites – pitfalls and some handy tips
12.30 - 1.30	Lunch			
1.30 - 3.00		Workshop: Characterisation and evaluation of vapour intrusion		Workshop: Health risk assessment of contaminated sites – pitfalls and some handy tips
3.00 - 3.30	Afternoon tea			
3.30 - 5.00		Workshop: Characterisation and evaluation of vapour intrusion		Workshop: Health risk assessment of contaminated sites – pitfalls and some handy tips
5.00 - 5.30	Welcome reception			
5.30 - 5.45		Official opening of the 4th International Contaminated Site Remediation Conference		
5.45 - 6.45		Mr Dennis Monahan - The commemorative Brian Robinson Lecture		

PROGRAM TIMETABLES

Program Sunday 11 September

Ballroom C		Suite 3		Balcony Room 4	
	Workshop: Science communication		Workshop: Software solutions in groundwater – introducing MIKE SHE and FEFLOW		Workshop: 1st National Forum and Workshop on fire-fighting foams and the environment
Morning tea					
	Workshop: Science communication		Workshop: Software solutions in groundwater – introducing MIKE SHE and FEFLOW		Workshop: 1st National Forum and Workshop on fire-fighting foams and the environment
Lunch					
	Workshop: Grant writing		Workshop: Software solutions in groundwater – introducing MIKE SHE and FEFLOW		Workshop: 1st National Forum and Workshop on fire-fighting foams and the environment
Afternoon tea					
	Workshop: Grant writing		Workshop: Software solutions in groundwater – introducing MIKE SHE and FEFLOW		Workshop: 1st National Forum and Workshop on fire-fighting foams and the environment
Welcome reception					
Official opening of the 4th International Contaminated Site Remediation Conference					
Mr Dennis Monahan - The commemorative Brian Robinson Lecture					

PROGRAM TIMETABLES

Program Monday 12 September

		Ballroom A			Ballroom B											
8.30 - 8.50	Permeable Reactive Barriers Session Chair: Sreenivasulu Chadalavada	A100	Scott Warner, AMEC Earth and Infrastructure	Two decades of application of PRBs to groundwater remediation: Major achievements and overview	Socio-Economic drivers for remediation Session Chair: Roel Plant	B100	Roel Plant, University of Technology, Sydney	Value-based land remediation – Opportunities for the remediation industry								
8.50 - 9.10			A101	Volker Birke, Ostfalia University		Impact of trace elements and impurities in technical grade zero valent iron brands on degradation of chlorinated ethenes in groundwater	B101	Gary Foster, URS-Scott Wilson, UK	Industrial symbiosis and the UK: The impact of the first 5 years of a nationally facilitated programme							
9.10 - 9.30							B102	Biruck D Yirsaw, CERAR, UniSA	Solidarity for environmental health in Ethiopia: A qualitative study of stakeholders' views							
9.30 - 9.50							A102	Wolf-Ulrich Palm, Leuphana University	PRBs for remediation of PAHs, BTEX and related contaminants	B103	Joanne Chong, University of Technology, Sydney	Value-based land remediation: A case study of EU-funded contaminated site rehabilitation of Lami dump, Fiji				
9.50 - 10.10										B104	Wil van Deur, CRC CARE	Understanding the policy process: Comparing lessons from the Netherlands and Australian experience				
10.00 - 10.40	Morning tea															
10.40 - 11.00	Permeable Reactive Barriers Session Chair: Volker Birke	A103	Ralph Ludwig, U.S. EPA	PRBs for treatment of chromium groundwater contamination	Socio-Economic drivers for remediation Session Chair: Roel Plant	B105	Jean-Paul Pearce, GHD	Effective risk communication to enable a school expansion on a site with elevated methane								
11.00 - 11.20			A104	Rick Wilkin, U.S. EPA		Groundwater arsenic treatment using permeable reactive barriers: An overview from field and laboratory testing	B106	Sean Shiels, EPA Victoria	A LCA-based approach to decision-making for contaminated sites							
11.20 - 11.40							A105	Ronald Giese, Groundwater Centre, Dresden, Germany	Reactive (oxygen) gas barrier and zone technology	B107	Aleta Lederwasch, University of Technology, Sydney	Opportunities for value creation: An institutional analysis of remediation decision-making processes at three Australian sites				
11.40 - 12.00										Panel discussion						
12.00 - 12.20										Discussion						
12.20 - 1.20	Lunch															
1.20 - 1.40	Permeable Reactive Barriers Session Chair: Scott Warner	A106	Franz-George Simon, BAM Federal Institute for Materials Research	Effective cleanup of groundwater contaminated with uranium using permeable reactive barriers	Emerging Contaminants Session Chair: Ming Wong	B108	Rao Surampalli, U.S. EPA	Emerging contaminants in the environment								
1.40 - 2.00			A107	Kandasamy Thangavadivel, CERAR, UniSA		Choosing the best design and construction technologies for permeable reactive barriers	B109	Annegret Biegel-Engler, Federal Environment Agency, Germany	Regulation of PFOA under REACH							
2.00 - 2.20							A108	James Stening, Orica Australia Pty Ltd	The history of Australia's first reactive iron barrier	B110	Jimmy Kao, National Sun Yat-Sen University	Assessment of sediment toxicity in Kaohsiung Harbor, Taiwan				
2.20 - 2.40										Discussion						
2.40 - 3.00																
3.00 - 3.40	Afternoon tea															
3.40 - 4.00	Permeable Reactive Barriers Session Chair: Volker Birke	A109	Sreenivasulu Chadalavada, CRC CARE	Groundwater modelling using PRBs: General aspects, case studies	Emerging Contaminants Session Chair: Rao Surampalli	B111	Ming Hung Wong, Hong Kong Baptist University, Hong Kong	Sources, fates and effects of emerging chemicals, with emphasis on the Pearl river delta, one of the world's mega deltas								
4.00 - 4.20			A110	Keely Mundle, Golder Associates					Sequenced PRBs system for the pre-treatment of nitrate and remediation of TCE	B112	Sophie Rocks, Cranfield University	Nanomaterials and policy – The influence of risk on the development of policy in areas of emerging risks				
4.20 - 4.40																
4.40 - 5.00																
5.00 - 6.00	Drinks and poster session															

PROGRAM TIMETABLES

Program Monday 12 September

Ballroom C				Suite 3			
Innovative site assessment tools	Session Chair: Peter Beck	C100	Luke Cattlin, Tonkin and Taylor Pty Ltd	Confirmation of the use of innovative site assessment tools: X-ray fluorescence	Minerals Industry Summit		Minerals Industry Summit
		C101	Camillo Coladonato, Environmental Resources Management (ERM)	Using real time tools to develop higher quality conceptual site models			
		C102	Lowell Kessel, Environmental Remediation Resources Pty. Ltd.	Stable isotope probing to document biodegradation under monitored natural attenuation conditions			
		C103	Sven Hoffmann, URS Australia Pty Ltd	Plugging the gaps: A groovy conceptual site model and how to validate it			
		C104	Hui Tan, CERAR, UniSA	Anionic surfactant biosensor based on gold electrode and organic-inorganic hybrid material			
Morning tea							
Innovative site characterisation and assessment	Session Chair: Peter Di Marco	C105	David Dangerfield, AECOM	Fire damaged asbestos: Case study part two - Remediation of asbestos in soil	Minerals Industry Summit		Minerals Industry Summit
		C106	Peter Beck, GHD	Composite samples: Do they offer value when considering average exposure concentration over decision areas?			
		C107	Mark Britton, DHI Water and Environment Pty. Ltd.	The role of numerical flow and transport models as decision support systems in remediation projects			
		C108	Victor Arias Espana, CERAR, UniSA	Before and after purge sampling, is there any difference?			
		C109	Edward Wu, Coffey Environments	Applying numerical methods to improve low flow sampling technique			
Lunch							
Innovative site characterisation and assessment	Session Chair: Cheryl Lim	C110	Stephen McKeown, GHD	Contamination assessment of a fuel pipeline in NSW: the challenge of multiple sources of contamination in a heavy industrial area	Minerals Industry Summit		Minerals Industry Summit
		C111	Leigh Sullivan, Southern Cross University	A new method for assessing acid neutralising capacity in acid sulfate soil materials			
		C112	Chamindra Vithana, Southern Cross University	Underestimation of retained acidity measured using the net acid soluble sulfur (SNAS) method in acid sulfate soils containing schwertmannite and jarosite			
		C113	David Springer, Envirolab Group	The dangers of using ice in sample eskies			
		C114	Vishnu Pareek, Curtin University	Vulnerability of indoor air to airborne threats released inside a building			
Afternoon tea							
Innovative site characterisation and assessment	Session Chair: David Springer	C115	Geoff Anderson, ALS Environmental Division	Groundwater analysis: Minimising false positives and negatives - A key step in effective groundwater remediation	Minerals Industry Summit		Minerals Industry Summit
		C116	Peter Beck, GHD	Causes and effects of random variance in spatial data sets and effects on reliability of contamination distribution interpretation			
		C117	Andrew Kohlrusch, GHD	Contaminated site assessments: It's more than just numbers			
		C118	Camillo Coladonato, Environmental Resources Management (ERM)	High resolution site characterisation: An innovative approach to site investigations to support effective decision making			
Drinks and poster session							

PROGRAM TIMETABLES

Program Tuesday 13 September

		Ballroom A			Ballroom B						
9.00 - 10.00		A112	Plenary Speaker		TBC						
10.00 - 10.40 Morning tea											
10.40 - 11.00	eWaste Session Chair: Andrew Beveridge	A113	Kenneth Sajwan, Savannah State University	Electronic waste and its management in developing nations	Sustainable Remediation Session Chair: John Hunt	B113	Paul Nathanail, University of Nottingham, UK	Sustainable remediation: Emperor's clothes, technicolour dreamcoat or baroque grotesque?			
11.00 - 11.20											
11.20 - 11.40			A114				Suthipong Sthiannopkao, National Cheng Kung University	Comparison of eWaste management strategies between developed and developing countries	B114	Jonathan Smith, Shell Global Solutions, UK	Benchmarking of sustainable remediation decision-support tools used in a tiered sustainability appraisal framework
11.40 - 12.00			A115				Masahiro Oguchi, National Institute for Environmental Studies, Japan	Characterisation and flow analysis of substances contained in eWaste in Japan for better management in future	B115	Peter Nadebaum, GHD	Do our clean up-projects currently accord with the concept of sustainable remediation?
12.00 - 12.20			A116						B116	Kevin Simpson, URS Australia Pty Ltd	A net benefit approach to determining endpoints for active remediation systems
12.20 - 1.20 Lunch											
1.20 - 1.40	eWaste Session Chair: Kenneth Sajwan	A117	Ming Man, Hong Kong Baptist University, Hong Kong	Release of persistent toxic substances from uncontrolled eWaste recycling and actions for our future	Sustainable Remediation Session Chair: Peter Nadebaum	B117	Graeme Paton, The University of Aberdeen, UK	Decision support tools for sustainable remediation strategies: Concept to application			
1.40 - 2.00			A118				Yu Bon Man, Hong Kong Baptist University	Health risk assessment of abandoned farm soils after changing land use in Hong Kong, one of the world's mega cities	B118	David Tully, Coffey Environments	Prospects for the utilisation of in-situ thermal remediation techniques in Australia
2.00 - 2.20			A119				Peeranart Kiddee, CERAR, UniSA	Heavy metals and polybrominated diphenyl ethers (PBDEs) in leachates from Australian landfills: Implications to electronic waste	B119	John Hunt, Thiess Services Pty Ltd	Sustainability metrics for a range of thermal remediation methods
2.20 - 2.40			A120				Janet Chan, The University of Hong Kong	Body loadings and health risk assessment of dioxins at an intensive electronic waste processing site in China	B120	Luke Cattlin, Tonkin and Taylor Pty Ltd	Sustainable remediation examples of groundwater contaminated with TCE in a fractured rock aquifer
2.40 - 3.00			A121				Guan Hua Xing, China National Environmental Monitoring Centre, China	Assessment of bioaccessibility of PCBs in different food using an in vitro digestion model	B121	Marc Centner, ALS Environmental Division	Reducing sample volumes for the analysis of organic compounds: Improving sustainability in remediation
3.00 - 3.40 Afternoon tea											
3.40 - 4.00	Remediation of Metals and Metalloids in Soils and Groundwater Session Chair: Erica Doner	A122	Mohammad Rahman, CERAR, UniSA	Concentration of arsenic in home grown vegetables	Sustainable Remediation Session Chair: Jonathan Smith	B122	Jonathan Ho, Parsons Brinckerhoff	Remediation optimisation: Operation and monitoring of active remediation systems at remote sites			
4.00 - 4.20			A123				Adam Wightwick, University of Queensland	Industry wide approaches to risk assessment: A case study of copper in Australian vineyards	B123	Peter Nadebaum, GHD	Sustainable management of contaminated sites: Evaluating the containment option
4.20 - 4.40			A124				Stephen McKeown, GHD	Remediation of a plume of acidic zinc contaminated groundwater in Yagoona, NSW			Discussion regarding contamination containment options
4.40 - 5.00			A125				Girish Choppala, CERAR, UniSA	A magic weed to weed out chromium contamination			
5.00 - 6.00 Drinks and poster session											

PROGRAM TIMETABLES

Program Tuesday 13 September

Ballroom C				Suite 3			
Morning tea							
Toxicological measurements and characterisation	Session Chair: Jack Ng	C119	Cheng Peng, University of Queensland	Development of a three dimensional hanging drop cell exposure system (HDCES) for toxicological studies	Regulators Meeting		Regulators Meeting
		C120	Faye Liu, University of Queensland	Hanging drop, a novo in-vitro air benzene exposure model			
		C121	Prakash Shiva, University of Queensland	Improved in-vitro toxicology of inhalable iron-rich particles from mining industries			
		C122	Kavitha Ramadass, CERAR, UniSA	Toxicity of used and fresh engine oils to earthworm survival and soil health			
		C123	Suresh Ramraj Subashchandrabose, CERAR, UniSA	Toxicity of PAHs and heavy metals alone and in combination to microalgae			
Lunch							
The effects of contaminants on human health	Session Chair: Ming Wong	C124	TW Wong, The Chinese University of Hong Kong	Effects of contaminants on human health and persistent organic pollutants in Hong Kong mothers	Regulators Meeting		Regulators Meeting
		C125	Paul Lam, Hong Kong Baptist University	Impact of environmental pollution on human health: Should health care delivery system be radically reformed?			
		C126	Jamal Hisham Hashim, United Nations University - International Institute for Global Health	Arsenicosis in Cambodia from exposure to arsenic in groundwater			
Afternoon tea							
The effects of contaminants on human health	Session Chair: Brian Priestly	C127	Eddy Zeng, Guangzhou Institute of Geochemistry, Chinese Academy of Science	Persistent organic pollutants in the Pearl River delta (south China): Environmental processes and potential health risk via seafood consumption	Regulators Meeting		Regulators Meeting
		C128	Jack Ng, University of Queensland	The effects of inorganic contaminants on human health: Case studies			
		C129	Mohammad Rahman, CERAR, UniSA	Arsenic induced health effects to humans via consumption of arsenic contaminated drinking water			
Drinks and poster session							

PROGRAM TIMETABLES

Program Wednesday 14 September

		Ballroom A			Ballroom B					
8.30 - 8.50	BHP Billiton - Hunter River remediation project	Session Chair: Carl Bagnall	A126	Allan Dann, BHP Billiton	The business case	Resource utilization	Session Chair: Ravi Naidu	B124	Keith Syers, Naresuan University	Management of phosphorus in organic amendments for sustainable production and environmental protection
8.50 - 9.10			A127	Brad Foot, BHP Billiton	Remediation design			B125	Nick Willenbrock, CL:AIRE	Definition of waste: Development industry code of practice
9.10 - 9.30			A128	Brad Foot, BHP Billiton	Operational challenges			B126	Ya-Feng Zhou, University of Queensland	Use of alum-derived water treatment sludge to remove heavy metals from aqueous solutions
9.30 - 9.50			A129	Carl Bagnall, BHP Billiton	Environmental risk management			B127	Anitha Kunhikrishnan, CERAR, UniSA	Mobility and phytoavailability of copper in the presence of recycled water sources
9.50 - 10.10			A130	Carl Bagnall, BHP Billiton	Statutory approvals management					
10.00 - 10.40	Morning tea									
10.40 - 11.00	BHP Billiton - Hunter River remediation project	Session Chair: Carl Bagnall	A131	TBC, CH2M HILL	Lead engineering designer perspective	Resource management	Session Chair: Nanthi Bolan	B128	Christine Blanchard, Local Government Association of Queensland	Waste management approaches to maximise reuse in natural disasters
11.00 - 11.20			A132	TBC, Thiess Services	Principal contractor perspective			B129	Ho Kyong Shon, University of Technology, Sydney	Substrate-specific solar light photocatalytic activity of titania produced from Ti-salt flocculated sludge
11.20 - 11.40			A133	Ross McFarland, AECOM	Independent site auditor's perspective			B130	Manoj Shrivastava, Bhabha Atomic Research Centre	Utilisation of distillery effluent for fertigation of sugarcane
11.40 - 12.00			A134	Carl Bagnall, BHP Billiton	Community and wider stakeholder engagement			B131	Dane Lamb, CERAR, UniSA	Phytocapping: An alternative technology for the sustainable management of landfill sites
12.00 - 12.20			Panel Q&A Session					B132	Dustin Moore, University of Technology, Sydney	Landfills: Sustainability costs and challenges of waste management
12.20 - 12.40										
12.40 - 1.40	Lunch									
1.40 - 2.00	Remediation case studies	Session Chair: Martin Wegner	A135	Joop Harmsen, Alterra	Spreading of slightly polluted sediment on agricultural land	Resources characterisation	Session Chair: Enzo Lombi	B133	Richard Haynes, University of Queensland	Use of organic amendments and residue mud to improve the properties of bauxite residue sand as a growth medium
2.00 - 2.20			A136	Mark Yetman, Indian and Northern Affairs, Canada	Remediating contaminated sites in northern Canada			B134	Danny Slee, National Measurement Institute	Analysis of PCBs in biosolids and other waste materials
2.20 - 2.40			A137	Fouad Abo, GHD	Groundwater remediation in newer volcanic basalt geology: Optimise the effectiveness of active remediation			B135	Erica Donner, CERAR, UniSA	Metal speciation and distribution in biosolids
2.40 - 3.00			A138	Adrian Heggie, Parsons Brinckerhoff	Remediating and managing risk at the Dubbo benzene/MTBE plume			B136	Yanju Liu, CERAR, UniSA	Composition of red mud varies depending on source refineries
3.00 - 3.40	Afternoon tea									
3.40 - 4.00	Remediation case studies	Session Chair: Sim Ooi	A139	Graham Hawkes, AECOM	Challenges overcome during the remediation of the Boral Brickworks site for residential redevelopment, Woonona NSW	Resource value-addition	Session Chair: Richard Haynes	B137	Nanthi Bolan, CERAR, UniSA	Enhancing soil carbon sequestration utilising compost
4.00 - 4.20			A140	Adrian Hall, GHD	Mead street, Birkenhead: Residential future for gasworks site poses challenges for auditor			B138	Oxana Belyaeva, University of Queensland	Use of organic amendments to improve the properties of coal fly ash as a growth medium
4.20 - 4.40			A141	Richard Bush, Southern Cross University	Lime assisted tidal exchange as a low cost technology for broad scale acid sulfate soil remediation			B139	Balaji Seshadri, CERAR, UniSA	Effect of coal combustion products on the leaching of phosphorus in soils
4.40 - 5.00			A142	Martin Wegner, Mull and Partners	The use of molasses for in-situ remediation of chlorinated hydrocarbon groundwater contamination			B140	Bo Xiao, Huazhong University of Science and Technology	A novel treatment of livestock waste using combined underground river digester with UASB system
5.00 - 6.00	Drinks and poster session									

PROGRAM TIMETABLES

Program Wednesday 14 September

Ballroom C				Suite 3					
Defence Symposium			Defence Symposium	Bioavailability of contaminants	Session Chair: Jose-Julio Ortega	D100	Lena Ma, University of Florida	Phosphate-induced bioavailability reduction of lead in contaminated soils	
						D101	Nick Basta, The Ohio State University	Use of in vitro or soil property models to assess toxic metal bioavailability in soil: Validation to support regulatory acceptance	
						D102	Kirk Semple, Lancaster University	Bioavailability/bioaccessibility of organic contaminants in soil: Fundamentals to application	
						D103	Albert Juhasz, CERAR, UniSA	Use of in vitro techniques to predict the relative bioavailability of arsenic, cadmium and lead via the incidental soil ingestion pathway	
Morning tea									
Defence Symposium			Defence Symposium	Bioremediation	Session Chair: Steve McGrath	D104	Jose-Julio Ortega-Calvo, Instituto de Recursos Naturales y Agrobiologia de Sevilla - CSIC	Designing strategies to increase bioavailability in bioremediation of PAHs	
						D105	Richard Bentham, Flinders University	Enhanced degradation of pyrene by an environmental isolate of <i>Bacillus megaterium</i> in the presence of diesel	
						D106	Sharyn Gaskin, Flinders University	Monitoring in situ bioremediation of hydrocarbon-contaminated soil at sub-antarctic Macquarie Island using microbial assays and FTIR	
						D107	Albert Juhasz, CERAR, UniSA	Can the extent of TPH and PAH bioremediation be predicted using bioaccessibility assays?	
						D108	Tanya Caceres, TC Environmental Consultancy	Hydrolysis of Fenamiphos and its toxic oxidation products by <i>Microbacterium</i> sp. in pure culture and ground water	
						D109	Louise Cartwright, Centre for Contaminant Geoscience	Bioremediation of gasworks tar: A NE England case study	
Lunch									
Defence Symposium			Defence Symposium	Bioremediation	Session Chair: Albert Juhasz	D110	William Butler, Environmental Resources Management (ERM)	Full-scale application of anaerobic bioremediation to remediate TCE in groundwater	
						D111	Elise Asquith, University of Newcastle	Comparative bioremediation of petroleum hydrocarbon-contaminated soil by biostimulation, bioaugmentation and surfactant addition	
						D112	Peter Moore, WSP Environment & Energy	Microcosm studies and advanced site diagnostics to assess in-situ remedial options of a mixed chlorobenzene and chlorinated ethene groundwater plume	
						D113	Philip Block, FMC Corporation	The intersection of chemical oxidation and bioremediation: The impact of persulfate on microbial populations	
Afternoon tea									
Plant based cleanup studies	Session Chair: Edward Wu	C130	Raj Shekhar Singh, Central Institute of Mining and Fuel Research	Ecological study of revegetated coal mine spoil of an Indian dry tropical ecosystem along an age gradient	In Situ Chemical Oxidation	Session Chair: Albert Juhasz	D114	George Hoag, VeruTEK Technologies	Surfactant enhanced in-situ chemical oxidation (S-ISCO®) of former gas works site in the United States
		C131	Sivakoti Ramana, Indian Institute of Soil Science	Phytoremediation of chromium contaminated soils by <i>Tuberose</i>			D115	Will Ellis, Environmental Resources Management (ERM)	Assessing the application of ISCO in the subsurface
		C132	Hui Ming, UniSA, CERAR	Distribution and phytosorption of nutrient in rhizoid of hybrid giant napier in saline/sodic soil: A greenhouse study			D116	Regin Orquiza, Environmental Earth Sciences	Remediation of chlorinated hydrocarbon impacted groundwater using in-situ chemical oxidation (ISCO), western suburb, Victoria
		C133	Thammared Chuasavathi, UniSA, CERAR	The phytoavailability of copper as affected by biosolids-based co-composted products			D117	David Tully, Coffey Environments	In-situ chemical oxidation for remediation of petroleum hydrocarbon impacted groundwater utilising innovative delivery and dispersion methodologies
Drinks and poster session									

PROGRAM TIMETABLES

Program Thursday 15 September

		Ballroom A			Ballroom B							
9.00 - 9.20	Nanotechnology for environmental remediation Session Chair: Enzo Lombi	A143	Steve McGrath, Rothamsted Research	Nanoparticle bioavailability, toxicity in terrestrial environments	Vapor intrusion: Sampling and assessment Session Chair: Sophie Wood	B141	Greg Davis, CSIRO Land and Water	Effects of soil layering and soil type on the flux and transient behaviour of hydrocarbon, chlorinated and ketone vapours				
9.20 - 9.40												
9.40 - 10.00			A144				Zuliang Chen, CERAR, UniSA		Synthesis, characterisation and environmental applications of iron-based nanoparticles	B142	Jackie Wright, Environmental Risk Sciences Pty Ltd	Establishing exclusion criteria from empirical data for assessing petroleum hydrocarbon vapour intrusion
10.00 - 10.20			A145				Åsa Jamting, National Measurement Institute		Multi-technique approach to size characterisation of nanoparticles	B143	Ruth Jarman, Parsons Brinckerhoff	Vapour intrusion modeling with biodegradation to support the assessment of human health risk at a contaminated site
10.20 - 10.50	Morning tea											
10.50 - 11.10	Nanotechnology for environmental remediation Session Chair: Prashant Srivastava	A146	Tian Zhang, University of Nebraska-Lincoln	Nanotechnology: Environmental applications and implications	Vapor intrusion: Sampling and assessment Session Chair: Greg Davis	B144	Bart Eklund, URS Corporation, USA	Evaluation of soil-gas sampling rate				
11.10 - 11.30												
11.30 - 11.50			A147				Enzo Lombi, CERAR, UniSA		Closing the gap in environmental risk assessment of nanomaterials through interdisciplinary method development	B146	Dane Egleton, Leeder Consulting Pty. Ltd.	Comparison of active and passive soil vapour sampling methods for subsurface vapour intrusion assessment
11.50 - 12.10			A148				Irene Lo, The Hong Kong University of Science and Technology		Application of magnetic nano/micro scale iron-based particles on wastewater treatment and soil/groundwater remediation: Effectiveness, regeneration and challenges	B147	Gemma Williams, AECOM	Determining the most appropriate sampling technique for assessment of volatile contaminant exposure
12.10 - 12.30										B148	Sophie Wood, Environmental Resources Management (ERM)	Evidence-based remediation decision-making for vapour intrusion risk from petroleum hydrocarbons
12.30 - 1.10	Lunch											
1.10 - 1.30	Micro and Nanotechnology for environmental remediation Session Chair: Irene Lo	A150	George Hoag, VeruTEK Technologies	A novel green synthesised catalyst system for hydrogen peroxide	Vapor intrusion: Sampling and assessment Session Chair: Jackie Wright	B149	Kenneth Kiefer, Environmental Resources Management (ERM)	Comparison of technologies for assessing vapour intrusion in future structures from subsurface sources: Case study with side-by-side measured flux and J&E modelling				
1.30 - 1.50			A151				Eric Njagi, University of Connecticut		Biosynthesis of iron and silver nanoparticles at room temperature using aqueous sorghum bran extracts	B150	Harry O'Neill, Beacon Environmental Services Inc.	The importance of applying strict QA/QC procedures in the field and in the lab to produce passive soil gas data that will simultaneously identify hot spots
1.50 - 2.10			A152				Binoy Sarkar, CERAR, UniSA		Organoclays for environmental remediation	B151	Gavin Stevenson, National Measurement Institute	Interlaboratory comparison of analysis of volatiles (including BTEX) in air samples
2.10 - 2.30			A153						Discussion	B152	Adrian Heggie, Parsons Brinckerhoff	Vapour intrusion risk assessment evaluated by multiple lines of evidence: A TCE case study
2.30 - 2.50										B153	Victoria Lazenby, URS Australia Pty Ltd	Case study: Remediation cost mitigation through appropriate soil vapour assessment
2.50 - 3.10										B154	Lowell Kessel, Environmental Remediation Resources Pty. Ltd.	Enhancing mass recovery rates of chlorinated solvent contaminated soil with advanced VOC condensation technology during soil vapour extraction
3.10 - 3.40	Afternoon tea											
3.40 - 4.40		A154	Brajesh Singh, University of Western Sydney	Emerging and genomic approaches in bioremediation								
4.50 - 5.00	Drinks and poster session											

PROGRAM TIMETABLES

Program Thursday 15 September

Ballroom C				Suite 3					
Risk based management and cleanup approaches	Session Chair: Bruce Kennedy	C134	Zoe Squire, AECOM	Accounting for chemical saturation and solubility limits in the derivation of site specific remediation criteria	Advances in chemical remediation	Session Chair: John Collins	D118	Renato Baciocchi, University of Rome	Design criteria of in-situ chemical oxidation
		C135	Barry Noller, Centre for Mined Land Rehabilitation	Risk assessment of heavy metals and metalloids from historical mine practices in the Leichhardt River and surrounding locations			D119	Pamela Dugan, Carus Corporation	Enhanced TCE DNAPL mass removal through surfactant and polyphosphate permanganate oxidation
		C136	Emma Walsh, CH2MHILL	Approach to groundwater remediation - London case study			D120	Eric Njagi, University of Connecticut	Mimicking nature: Oxidation of 2,4,6-Trichlorophenol with mixed valent manganese oxides (K-OMS-2)
		C137	John Frangos, Toxikos Pty Ltd	Overview of health based guideline values - Present and future trends					
Morning tea									
Risk based management and cleanup approaches	Session Chair: Jean Meaklim	C138	Benjamin Hardaker, AECOM	Are current and proposed asbestos in soil guidelines protective of human health?	Advances in chemical remediation	Session Chair: George Hoag	D121	Danny McDonald, Lane Piper Pty Ltd	An innovative use of chemical oxidation to treat PAH-impacted soils
		C139	Mike van Alphen, UniSA	Asbestos in air and soil			D122	John Collins, VeruTEK Technologies	Environmental microemulsion catalysis: A sustainable way forward for NAPL and pesticide remediation
		C140	Sanjay Garg, Shell Global Solutions (US) Inc	LNAPL transmissivity - The emerging metric for hydraulic recovery			D123	Homer Genuino, University of Connecticut	Photodegradation of surfactant-based crude oil-in-water emulsions
		C141	Chris Bailey, Tonkin and Taylor Pty. Ltd.	Management of soil and groundwater contamination in the context of satisfying CUTEP			D124	Pamela Dugan, Carus Corporation	Sustained-release permanganate reactive barriers for green and sustainable remediation of chlorinated solvents
		C142	Roger Klein	Tank farm risk assessment - Avoiding environmental contamination			D125	Annette Nolan, Enviropacific Services	Chemical immobilisation of complex co-contaminated industrial waste
Lunch									
Risk based management and cleanup approaches	Session Chair: Andrew Beveridge	C143	Frank Lame, Deltares	Risk-based remediation: Role of standardised methods in site management	Advances in remediation technology	Session Chair: Barry Noller	D126	Shoabin Wang, Curtin University	Removal of phenolic contaminants using sulfate radicals activated by supported cobalt catalysts
		C144	Kane Mitchell, Environmental Auditors	The problem of changing practices and decision making in contaminated sites management			D127	Jianhua Du, CERAR, UniSA	A comparison of mechanical rake and ultrasonics on restructuring clay aggregates
		C145	Peter Gringinger, Lane Piper Pty Ltd	Observations of the random approaches to remediation planning in Australia			D128	James Braham, Enviropacific Services	Tertiary water treatment process for contaminated groundwater
		C146	Bruce Kennedy, CRC CARE	Establishing an Australian-specific remediation framework			D129	Soon Kong Yong, CERAR, UniSA	Synthesis and characterisation of thiolated chitosan beads for wastewater remediation
		C147		Discussion			D130	Ruh Ullah, Curtin University	Visible light photocatalytic decomposition of toluene with BiMO ₄ (M = Ta, Nb)
					D131	Bithin Datta, James Cook University	Contaminated and coastal aquifers: Advances in source characterisation, monitoring network design, and optimal remediation strategy development		
Afternoon tea									
Drinks and poster session									

PROGRAM TIMETABLES

Poster Program

Balcony Rooms			
Monday 12 September	E100	Ruth Keogh, Parsons Brinckerhoff	Back to basics - Is your site assessment/ remediation program based on sound knowledge?
	E101	Paul Armishaw, National Measurement Institute	Proficiency testing of pesticides and hydrocarbon pollutants in water and soil: Review of recent results.
	E102	Akbar Forghani, University of Guilan	Comparison of two sequential extraction procedures for the fractionation of zinc in agricultural calcareous soils of Iran
	E103	Raktim Pal, CERAR, UniSA	MDMA degradation in soil
	E104	Lowell Kessel, Environmental Remediation Resources Pty Ltd	Mapping complex groundwater flow paths: Understanding preferential flow paths in aquifer materials with differing porosities
	E105	Kandasamy Thangavadivel, CERAR, UniSA	Zero-valent iron treatability study using trichloroethylene spiked deionised water yields rate constant considerably lower than that for a highly saline contaminated groundwater
	E106	Ka Lai Chow, Croucher Institute for Environmental Sciences and the Department of Biology, Hong Kong Baptist University	Photocatalysis for efficient treatment of flame retardants (PBDEs) by nano-sized TiO ₂
	E107	Olanrewaju Bello, University of Calabar	Effect of oil spillage on the properties of soil and environment around the marketing outlets of some petroleum marketing companies in Calabar Cross River state, Nigeria
	E108	Cameron McLean, Enviropacific Services	Remediation of a former steelworks, Alexandria NSW
	E109	Dane Lamb, CERAR, UniSA	Phytoavailability of barium in soils contaminated by barite
	E110	Akbar Forghani, University of Guilan	Fractionation changes of cadmium with time in soils treated with cadmium chloride in different moisture regimes

Balcony Rooms			
Tuesday 13 September	E111	Ebrahim Adhami, Yasouj University	
	E112	Hui Ming, CERAR, UniSA	
	E113	Manoj Shrivastava, Bhabha Atomic Research Centre	
	E114	Hafiz Chudhary, University of Agriculture, Faisalabad	
	E115	Md. Mezbau Bahar, CERAR, UniSA	
	E116	Peter Storch, URS Australia Pty Ltd	
	E117	Stephen McKeown, GHD	
	E118	Christian Wallis, Golder Associates	
	E119	Dawitt Bekele, CERAR, UniSA	
	E120	Peter Beck, GHD	
	E121	Dane Lamb, CERAR, UniSA	

PROGRAM TIMETABLES

Poster Program

The effect of cadmium and zeolite on growth and chemical composition of corn in a calcareous soil
Biodiversity of soil fauna in hybrid Giant Napier (HGN) plantation ecosystem
Phytofiltration of arsenic contaminated water using <i>Hydrilla verticillata</i>
Discovering plant-bacterial interaction to clean up petroleum contaminated soil
Arsenic bioremediation potential of <i>Variovorax</i> sp. Mm-1 isolated from soil
Recent advances in the remediation of soil and groundwater impacted by chromium ore processing residue
Remediation of a spent phosphoric acid catalyst waste site using stabilisation and phytoremediation
Sustainable remediation solution for lead shot impacted recreational reserve: Results from mechanical sieving and gravity separation field trial
Shallow vadose zone soil gas sampling for vapour intrusion risk assessment
Statistical approach to improving reliability and defensibility of bioaccessible fraction estimation
Bioaccessibility of Pb in different particle size fractions in long-term field contaminated soils: Implications for human health risk assessment

Balcony Rooms			
Wednesday 14 September	E122	Mostafa Chorom, Ahvaz University	Bioremediation of Ahvaz oil contaminated soil by oil-degrading bacteria and arbuscular mycorrhizal
	E123	Alan England, SAS Water Solutions	Two stage reduction of phenols in wastewater: Ozone oxidation and bacterial degradation
	E124	Thammared Chuasavathi, CERAR, UniSA	Immobilisation of copper in copper mine soil using biosolids-based co-composted products
	E125	Sifau Adejumo, University of Ibadan	Comparative effects of compost and inorganic fertiliser on lead transport and accumulation in maize crop grown on heavy metal contaminated soil in Nigeria
	E126	Jaeyeob Jeong, Department of Forest Resources	Carbon input by litterfall and soil respiration of a red pine stand with varying degree of damage from pine wilt disease
	E127	Ramya Thangarajan, CERAR, UniSA	Nitrous oxide emission from organic amendments
	E128	Thavamani Palanisami, CERAR, UniSA	Metal tolerant PAH degrading bacteria: Patterns of metal tolerance and environmental relevance
	E129	Anitha Kunhikrishnan, UniSA, CERAR	Effect of recycled water sources on the bioavailability of copper to earthworms and microorganisms
	E130	Jarupong Prasopsuk, Office of Agricultural Research and Development Region 3, Development of Agricultural, Khon Kaen	Pesticide residues in compost and vermicompost from organic waste in northeast Thailand
	E131	Andromeda Wong, The Chinese University of Hong Kong	A review of organic pollutant exposure studies in China & Hong Kong: Dioxins in human milk

TECHNICAL TOURS

Technical tour 1: Sustainable resource management

Date: Friday 16 September 2011
Time: 8:30am – 5:30pm
Departure: Victoria Square in front of the Hilton Adelaide hotel
Cost: \$120 per person

Registration fee includes registration, materials and handouts and lunch at the Watershed Function Centre at Mawson Lakes. This full-day tour will depart from the Adelaide Hilton hotel at 8.30am, and return at approximately 5.30pm. Participants on the Technical Tour will need to wear enclosed shoes, trousers and long sleeved shirts for the site visits. Other safety equipment will be provided at the individual sites as required. An outline for the Technical Tour is as follows:

Tour itinerary	
8:30am	Bus to depart Hilton Adelaide hotel
9:00am – 9:45am	E-Cycle Recovery
10:15am – 10:45am	Morning tea/Tour of CERAR labs
11:30am – 12:30pm	Jeffries Recycling Facility
1:00pm – 3:00pm	Lunch – Watershed Function Centre
3:30pm – 4:30pm	City of Salisbury water treatment systems
5:30pm	Return to Hilton Adelaide hotel (arriving at approximately 5.30pm)

Technical tour 2: Remediation technologies for contaminated soil and groundwater

Date: Friday 16 September 2011
Time: 8:30am – 5:30pm
Departure: Victoria Square in front of the Hilton Adelaide hotel
Cost: \$120 per person

Registration fees include registration, materials and handouts and lunch at the Watershed Function Centre at Mawson Lakes. This full-day tour will depart from the Hilton Adelaide hotel, at 8.30am and return at approximately 5.30pm. Participants on the Technical Tour will need to wear enclosed shoes, trousers and long sleeved shirts for the site visits. Other safety equipment will be provided, as required, at the individual sites. An outline for the Technical Tour is as follows:

Tour itinerary	
8:30am	Bus to depart Hilton Adelaide hotel
9:00am – 10:00am	Bioremediation of TCE-contaminated water, Edinburgh Defence Site
10:45am – 11:15 am	Morning tea/Tour of CERAR labs
11:30 – 12:30pm	S-ISCO field trial, Edinburgh
1:00pm – 3:00pm	Lunch – Watershed Function Centre
3:30 – 4:30pm	AFFF Wastewater Treatment Plant, Edinburgh Defence Base
5:30pm	Return to Hilton Adelaide hotel (arriving at approximately 5.30pm)

4th International Contaminated Site Remediation Conference

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TWO DECADES OF APPLICATION OF PRBs TO GROUNDWATER REMEDIATION: MAJOR ACHIEVEMENTS AND OVERVIEW

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This year – 2011 – marks the 20th year anniversary of the first pilot testing of the permeable reactive barrier (PRB)¹ as an in situ groundwater remedy by University of Waterloo researchers at the Canadian Forces Base (CFB) Borden site in Ontario, Canada. Over the ensuing 20 years, the PRB concept would evolve from its standing as an “innovative” remedy for chemically-impacted groundwater first commercially applied at a former semiconductor manufacturing facility in northern California, USA to a “developed” technology that has been installed at sites around the globe as well as being identified as one of the most sustainable groundwater treatment remedies available. Furthermore, over the past two decades, this remediation concept grown to be the subject of research at many academic institutions, has become a common-place addition to feasibility studies and alternative analysis documents for remediation projects, and has been the specific focus of technical short courses and conferences spanning the 1995 special session on PRBs at the American Chemical Society annual meeting in California, USA to internet-based short-courses sponsored by the U.S. Environmental Protection Agency, to international meetings in the United Kingdom, Germany, and Italy, to today’s Clean Up II conference in New South Wales, Australia. Considering that the first full-scale commercial PRB composed of ZVI was installed in November 1994 and continues to function, the proof that this remedial approach is truly one of the more sustainable and resource conservative treatment concepts for chemically-affected groundwater is founded.

Although exact wording has morphed over the past two decades, the generally accepted definition of a PRB, as modified from ITRC (2005) is:

an engineered, continuous, in situ permeable treatment zone designed to intercept and remediate a contaminant plume

Historically, the PRB has taken additional descriptive names including “permeable treatment zone,” “applied reactive treatment zone,” “permeable reactive treatment zone,” etc. From these names and definition, it is clear that the treatment of contaminated groundwater occurs within the PRB, or immediately adjacent to it (for example, the evolution of hydrogen from a ZVI-based PRB may enhance biodegradation processes a short distance down gradient from the PRB). This recognition is important because the PRB, by itself, would not completely remediate a contaminant plume until all affected groundwater at a site flows through the PRB. More accurately, the primary use of a PRB is to eliminate or substantially reduce the mass flux of the target contaminant(s) to areas located immediately downgradient of the PRB alignment. The PRB is not, in its typical intent, used as a *source remediation* technology; but is more correctly a *source control* remediation technology. The PRB may also be used as a *receptor protection* technology if its primary purpose is to protect sensitive receptors located either near or far from a potential contaminant source.

A key acknowledgement proven over 20 years is that each PRB application is unique in all characteristics – design, objectives, construction, economics, monitoring and specific

¹ Composed of zero valent iron (ZVI)

performance. One supporting reason for this is that each remediation site is unique with respect to site geology and hydrogeology, contaminant occurrence and distribution, land use issues, and regulatory drivers. This uniqueness is both an advantage and disadvantage for PRB application. As an advantage, because the PRB is not an “off-the-shelf” remedy, it must be designed to suit the needs of the site. This has led to the identification and development of multiple installation methods (e.g., excavate and fill, injection and jetting, single pass trenching and replacement, large diameter boring emplacements) and geometries (e.g., continuous wall, funnel and gates, multi-discrete depth application, dual walls, etc.), and the identification and use of different treatment media (beyond ZVI) for a variety of chemicals (for and beyond chlorinated hydrocarbons). For example, PRB treatment materials in addition to ZVI have ranged from bioactive mulch, to crushed limestone, to zeolite minerals with contaminants treated ranging from chlorinated hydrocarbons, to dissolved reducible metals, to radioactive constituents such as strontium-90. Research continues in various institutions to develop better technical understanding of many of the specific treatment mechanisms to not only develop treatments for more chemical types, but also to better understand longevity of a given treatment type so that appropriate contingencies can be invoked before PRB performance is reduced beyond the objectives of a project

The two key technical components for PRB performance consist of the hydraulic routing system and the chemical treatment system. The ability of the hydraulic design to move affected water through the PRB so that the required treatment occurs is also the more difficult of the two technical components to design. For this reason, PRBs that have been reported to be underperforming mostly cite poor hydraulic performance as the root problem. Efforts to design PRBs for better and reliable hydraulic performance rely on the collection of quality characterization information as well as assuring that both design details and construction methods are appropriate to meet the functional objectives of the system.

Assessing the long-term performance of the PRB continues to be a key area of evaluation for both current and future PRB installments. Performance data is not readily available for many PRB installations, and detailed information for those PRB sites that do report is often difficult to collect. As PRBs continue to age, the collection and analysis of this type of data – both hydraulic and chemical – will be key activities to best monitor sites before failures occur and develop successful PRB applications.

Over the next 10 to 20 years, the PRB concept is anticipated to evolve further thanks to the expected access to and evaluation of additional technical and economic performance, and the continuing research and development into more advanced implementation and monitoring methods to assure longevity and successful system performance over many decades.

IMPACT OF TRACE ELEMENTS AND IMPURITIES IN TECHNICAL GRADE ZERO VALENT IRON BRANDS ON DEGRADATION OF CHLORINATED ETHENES IN GROUNDWATER

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Zero valent iron (ZVI) permeable reactive barriers (PRBs) as well as direct application of nano and/or micro scale ZVI emulsions (NZVIs) by injection are effective in situ technologies for remediating ground water plumes or source zones, resp., which are contaminated by chlorinated volatile organic compounds (cVOCs) or certain heavy metals. However, ZVI or NZVI types used for these purposes so far have actually been produced chiefly for entirely different industrial applications rather than application for groundwater remediation, i.e., they do not represent tailored reagents regarding their application to remediating contaminated sites. All ZVI or NZVI types which have been applied so far to reductively dechlorinate cVOCs in contaminated ground water are of technical grade, i.e., especially regarding PRBs, very often made from scrap metal of different origins, compositions etc., or regarding NZVIs, are originally produced for application in the electronic or even food industry only, therefore very often associated with different kinds and amounts of trace elements. Thus, their reactivity regarding cVOC dehalogenation in ground water can vary significantly, which has already been addressed and documented extensively (Johnson et al., 1996; Miehr et al., 2004; Ebert et al., 2006). This contribution describes investigations and first results of a study which has been performed during the second operational term of the German research and development (R&D) PRB program "RUBIN" between 2006 and 2011 (Birke et al., 2004; Birke et al., 2005; RUBIN, 2011), to address this issue in order to achieve an improved quality assurance regarding proper practical field scale implementations of different ZVI and NZVI brands and particular production batches of them.

Using long term column and short term batch experiments as well as electrochemical investigations, the impact of different technical ZVI brands (at nano scale as well as coarser qualities to be used in PRBs) *as well as different ZVI production batches from the same supplier* on the reductive dechlorination efficacy regarding tetrachloroethene (PCE) in ground water has been investigated. It was found that trace elements and local surface elements do vary significantly regarding kind and amounts, and they may have a significant impact on the degradation efficacy. Hence, a protocol being useful for practical applications/implementations is required to properly and effectively select the right ZVI or NZVI type as well as its right production batch *shortly prior to* its particular field scale application in a ZVI PRB or regarding injecting NZVIs. This would especially be useful when feasibility tests have been performed significantly earlier to the actual field application, i.e., wherein a *different* production batch of the same ZVI type/brand might have been used/checked earlier in the lab rather than it is later applied in the field. A test protocol may prevent applicants/stakeholders (especially vendors and site owners) from facing a potentially serious failure at the very early start of a field scale application using ZVI or NZVI, simply because of applying perhaps the "wrong" production batch. Furthermore, these investigations may deliver a significant contribution to improved planning of field scale applications of ZVI PRBs as well as injections of NZVIs in the future.

Different batch experiments using one ZVI production batch (Gotthart-Maier, Rheinfeld, Germany) were performed in comparison to a column experiment using the same production batch. It could be found (FIGURE 1) that a good correlation between the applied amount of ZVI and the pseudo first order rate constant $k(\text{obs})[1/\text{h}]$ can be attained. These findings are virtually independent of the stirring rate, as FIGURE 1 reveals. In the corresponding column experiment, $k(\text{obs})$ could be determined at 0,05 1/h after around 20 pore volumes (the very

first pore volumes show adsorption and not degradation, which is a very common observation for technical ZVI brands regarding column or batch studies), corresponding to an average load of Fe in a batch experiment at around 20 g/L.

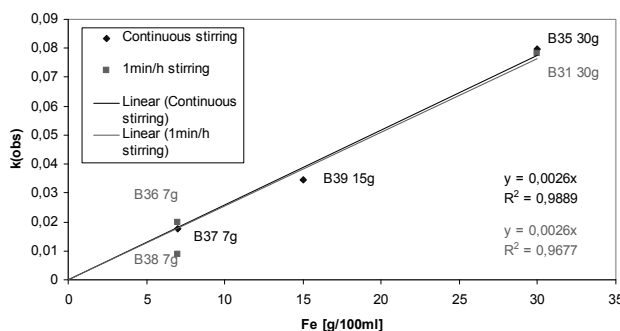


FIGURE 1. Linear relationship between $k(\text{obs})$ [1/h] and Gotthart-Maier ZVI mass employed in batch experiments using PCE in contaminated ground water from the Rheine PRB site in Germany at 10 °C. Values are virtually independent of the stirring rate/duration of stirring (using an overhead stirrer/shaker). Data points represent a single batch experiment (“B” and experiment number and the amount of a certain Gotthart-Maier ZVI production batch per 100 ml).

Basing upon these findings, a provisional recommendation for a quality assurance test protocol can be outlined (further validation is currently underway to prove the concept using different other ground water types etc.): regarding the very column experiment, which shows the best performance (therefore the ZVI brand used therein will most probably be selected for the later field scale application), batch experiments should be performed in parallel by applying 3-4 different amounts of the same ZVI or NZVI brand and production charge in order to assign $k(\text{obs})$ of the column experiment (after 20-30 pore volumes) to a specific amount/portion of ZVI which is required in the batch experiment to show approximately the same value. If the batch experiment is repeated later again using the actual (differing) production charge of ZVI or NZVI to be charged into a field scale PRB or to be injected into an aquifer, resp., and it shows nearly the same value of $k(\text{obs})$, there would be no concern to actually apply it in the field. If $k(\text{obs})$ were significantly lower, i.e., in the order of one decimal power or more, one should be cautious regarding applying this production charge in the field. Further investigations had to be taken into account.

REFERENCES

- Birke, V., Burmeier, H., Niederbacher, P., Hermanns Stengele, R., Koehler, S., Wegner, M., Maier, D., Eggers, J., Maier, J., Hofmann, B., Kühlers, D., Weindl, J. and Koch, M. (2004). PRBs in Germany, Austria, and Switzerland: Mainstreams, Lessons Learned, and New Developments At 13 Sites After Six Years. *Paper 3A-14*, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds —2004*. Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2004). ISBN 1-57477-145-0, Battelle Press, Columbus, OH.
- Birke, V., Burmeier, H., Dahmke, A., und Ebert, M. (2005). The German Permeable Reactive Barrier (PRB) Network „Rubin“: Temporary Overall Results and Lessons Learned after five Years of Work“, CONSOIL 2005 (9th International FZK/TNO Conference on Contaminated Soil), Bordeaux, France, 03-07 October 2005 (computer optical disk), 2865-2887
- Ebert M., Köber R., Parbs A., Plagentz V., Schäfer D., Dahmke A. (2006). Assessing degradation rates of chlorinated ethylenes in column experiments with commercial iron materials used in permeable reactive barriers. *Environ. Sci. Technol.*, 40(6), 2004-10.
- Johnson, T.L., Scherer, M.M., und Tratnyek, P.G. (1996). Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.*, 30(8), 2634-2640.
- Miehr R., Tratnyek P.G., Bandstra J.Z., Scherer M.M., Alowitz M.J., and Bylaska E.J. (2004). Diversity of contaminant reduction reactions by zerovalent iron: Role of the reductate. *Environ. Sci. Technol.* 38, 139-147.
- RUBIN (2011). <http://www.rubin-online.de> (accessed July 1st, 2011)

PRBs FOR REMEDIATION OF PAHs, BTEX AND RELATED CONTAMINANTS

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INTRODUCTION

The ability of activated carbons (AC) in the remediation of PAHs, BTEX, phenols and related aromatic compounds in general is well known. In addition NSO-heterocycles are important constituents of tar oils and are always found together with PAHs in PAH-contaminated samples. Starting 2000, the Federal Ministry of Education and Research in Germany (BMBF) funded the project RUBIN (German Permeable Reactive Barrier Network) and in continuation RUBIN II has been launched 2006. Investigations within RUBIN II (subproject 3) were carried out to assess the efficiency of activated carbons in permeable reactive barriers (PRB) in the remediation of especially NSO-heterocycles. To achieve the goals of the project, accompanying and necessary measurements concerning properties, analytical methods, and adsorption behavior and concentration levels of NSO-heterocycles in comparison to PAHs, phenols and related aromatic compounds were performed. The remediation of organic compounds using activated carbon in two Permeable Reactive Barriers were investigated in field campaigns.

METHODS

Besides obviously necessary compounds such as the EPA-PAH and the short-chained alkylated phenols alkylated PAH and NSO-heterocycles, usually found in groundwater, were incorporated into the list of about 100 compounds analyzed. Analysis was performed using GC-headspace, GC-MS, HPLC-DAD, HPLC-fluorescence and HPLC-MS/MS.

In order to gain the basic knowledge required to assess adsorption processes, batch experiments to determine adsorption isotherms on activated carbon were obtained for selected PAHs, NSO-heterocycles and related compounds. Besides single compounds, multi-component mixtures were investigated and a method to fit the complex concentration dependences was developed.

Column experiments were performed with artificial mixtures and real groundwater to determine break-through curves and to establish a ranking for a variety of PAHs, phenols and NSO-heterocycles. Results of column experiments were compared with corresponding batch experiments.

Besides the analysis of tar oils and contaminated ground waters especially four field campaigns were accomplished at two established PRBs in Austria (Brunn am Gebirge) and in Germany (Karlsruhe) between November 2007 and October 2009. Concentrations were used to assess the efficiency of PRBs to remediate the organic compounds investigated.

RESULTS AND DISCUSSION

Isotherms and comparison of activated carbons

For N-heterocycles (N-HET) the adsorption parameter K (Freundlich isotherm at $T \pm \sigma = 20 \pm 3$ °C, AC Epibon Y12x40 from Donau Carbon) was found to be always lower compared to the parent PAH (i.e. quinoline and iso-quinoline versus naphthalene or phenanthridine versus phenanthrene). In addition, the few examples available suggest the order $K(S-HET) > K(O-HET) > K(N-HET)$, fulfilled for all compounds investigated.

Six activated carbons were compared with respect to their adsorption capacities for six representative compounds (phenol, benzene, toluene, benzofuran, 2-methylquinoline and benzothiophene). A rough order with respect to the adsorption parameter K (Freundlich

isotherm) was obtained: AC(30N, Donau Carbon)~AC(Epibon, Donau Carbon) < AC(ROW, Norit) < AC(F200, Chemviron) < AC(1240, Norit) ~AC(F400, Chemviron). However, relative standard deviations of K vary by 20-25 % only, surprisingly similar for all compounds. Although activated carbons were found to be definitely different, activated carbons investigated turned out to be more similar than previously assumed.

Column experiments

Columns used were made of stainless steel with PTFE tubings for influent, effluent and sampling ports with column diameter: 27.6 mm, length: 267 mm and filled with 76 g of AC. In column experiments “biotic” and “abiotic” scenarios were realized using AC Epibon Y12x40 (Donau Carbon) at $T \pm \sigma = 12 \pm 2$ °C with real ground water. Front velocities (defined as mg loaded activated carbon per hour) for both columns are comparable and it was not possible to detect differences for any compound within statistical uncertainties. Nevertheless, for the “abiotic column” any potential biological degradation was inhibited using sodium azide. Hence, processes on this column, although using real ground water, are not influenced by degradation reactions of microorganisms and pure adsorption is observed. The order of compounds, sorted by front velocities were used to rank all compounds with respect to their adsorption behavior. Qualitatively and as assumed phenol and benzene are the worst adsorbing compounds, pyrene and fluoranthene the best. Most worst adsorbing heterocycles in the mixture used were benzofuan (O-heterocycle), benzothiophene (S-heterocycle) and isoquinoline (N-heterocycle).

Efficiencies of permeable reactive barriers

Karlsruhe (Germany)

Although sum concentration in one of the most contaminated zones in Karlsruhe is in the range of 1800 µg/L, influent concentrations at the gates of the barrier are low with maximum values in the range of 50 µg/L. Moreover most of the mass (about 90 %) at the gates is determined by acenaphthene. Heterocycles are present in the main contaminated region by about 16 % but play no role at the gates with concentrations below 1 µg/L. Nevertheless, for all compounds effluent concentrations were found to be below detection limits and the efficiency of the PRB is > 98 % after more than 8 years of operation.

Brunn am Gebirge (Austria)

The main plume direction concentrates on gate 2 with a very high sum concentration of about 5600 µg/L. Sum concentrations at the neighboring gates 1 and 3 are a factor 100 (gate 3) and factor 1000 (gate 1) lower. The fraction of NSO-heterocycles at gate 3 is about 7%, predominantly determined by benzothiophene (180 µg/L), dibenzothiophene (120 µg/L) and carbazole (50 µg/L). As is the case for the PRB in Karlsruhe in Germany, effluent concentrations were found to be below detection limits for all compounds and the efficiency of the PRB is > 99 % for more than 9 years of operation.

CONCLUSIONS

Batch experiments and column runs in the laboratory using artificial solutions and real ground waters supported results found in field campaigns. Adsorption isotherms on activated carbons (using especially Epibon Y12x40 from Donau Carbon) were obtained from batch experiments for single compounds and mixtures. In addition, Freundlich parameters for both experimental setups were compared with column runs. From the results obtained general conclusions can be drawn for the design and operation of reactive barriers using activated carbon. In the two PRB investigated a remediation of more than 98% was found in all measurement campaigns. The successful remediation was obtained even after years of operation. The concept of PRB with activated carbon as adsorbent thus appears suitable for the removal of aromatic compounds, even for NSO-heterocycles.

TREATMENT OF Cr6 IN GROUNDWATER USING PRB SYSTEMS

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INTRODUCTION

Hexavalent chromium (Cr6) is a relatively ubiquitous contaminant found at nearly half of all Superfund sites in the USA. Technologies for treating Cr6 in groundwater generally focus on promoting reducing conditions to convert Cr6 to the relatively immobile and non-toxic trivalent (Cr3) form. Reducing conditions can be induced using permeable reactive barriers (PRBs) in the form of trench-and-fill systems, chemical redox curtains or organic carbon based biotic treatment zones.

PRB OPTIONS FOR TREATMENT OF Cr6

Trench-and-Fill Systems

Likely the most effective media for treating Cr6 in trench-and-fill applications is granular ZVI (ZVI filings). ZVI very rapidly converts Cr6 to Cr3 abiotically both at the ZVI surface and in reactions with Fe(II) generated from oxidation of the ZVI. Less costly alternatives to ZVI include organic substrates such as compost or mulch that can be employed to promote microbially-mediated Cr6 reduction. The use of organic substrates as PRB media, however, is likely to be less dependable due to difficulties in maintaining the long-term integrity of the PRB. In addition, organic carbon based PRBs lack the longevity of ZVI-based systems. The earliest and most studied trench-and-fill PRB for treatment of Cr6 in the USA has been a full-scale ZVI PRB installed in 1996 at Elizabeth City, North Carolina (Wilkin et al., 2005). This PRB, constructed to a depth of 10 m, length of 46 m and width of 0.6 m using a continuous trencher, has been successfully treating Cr6 in groundwater at concentrations up to ~15 mg/L for over 15 years. Annual performance monitoring of this PRB has indicated no signs of impending failure suggesting the PRB is likely to continue performing well for the foreseeable future. Low TDS levels and low dissolved oxygen concentrations in the influent water have contributed significantly to the longevity of the PRB.

Chemical Redox Curtains

Chemical reductants are injected into the subsurface to promote abiotic reduction of Cr6 and generally take the form of reduced sulphur compounds (e.g., sodium dithionite, calcium polysulphide) or ferrous iron compounds (e.g. FeCl₂, FeSO₄). Reduced sulphur compounds tend to react more rapidly with Cr6 at lower pH values while ferrous iron reacts more rapidly at higher pH values. Chemical reductant injection tends to be a cheaper and more flexible option (e.g. no depth limitations) relative to ZVI trench-and-fill systems but may not be as dependable. Chemical reductants are generally injected along a line of wells oriented perpendicular to groundwater flow to ideally create a continuous redox curtain. Chemical reductants can both directly treat dissolved and solid phase Cr6 in the impacted aquifer formation as well as convert solid phase iron to ferrous iron thereby imparting an extended residual treatment capacity to the aquifer solids. Injectable chemical reductants are generally not as persistent in the subsurface as trench-and-fill media and will generally need to be reapplied periodically to sustain long-term treatment of Cr6 plumes.

A well documented application of a chemical reductant is the use of sodium dithionite (hydrosulfite) at the US Department of Energy Hanford site to treat a large Cr6 plume (Szecsody et al., 2004). Sodium dithionite buffered with carbonate was injected into the subsurface formation at the site to convert solid phase aquifer iron to the ferrous iron form. Although initial success was observed, breakthrough of Cr6 began to eventually occur at locations where aquifer solid phase iron concentrations were apparently not sufficiently high.

A variation of the dithionite technology, applied at a Cr6-impacted Superfund site in South Carolina, involved injection of sodium dithionite in combination with ferrous sulphate to ensure an adequate supply of ferrous iron for long-term treatment (Ludwig et al., 2007). Five-year data from this site has indicated sustained treatment of the Cr6 plume with treatment longevity being at least partially attributed to the relatively low dissolved oxygen concentrations in the Cr6-impacted groundwater.

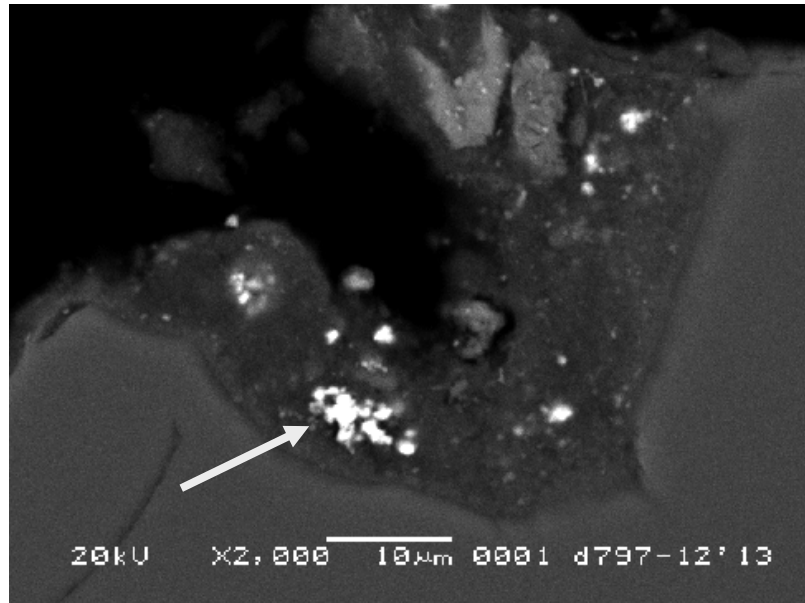


Fig. 1. Iron sulphide (white precipitate) formed on aquifer solid surface following treatment of aquifer formation with sodium dithionite + ferrous sulphate.

Organic Carbon Injection

Injectable organic carbon substrates to promote microbially-mediated reduction of Cr6 include compounds such as lactate, molasses, corn syrup, and ethanol. Organic carbon substrates require a higher injection frequency relative to chemical reductants but are generally cheaper to apply. A well publicized site in the USA where organic substrates have been employed is the Pacific Gas & Electric site in Hinkley, California (subject of the film *Erin Brockovich*). Lactate was initially used and was replaced with ethanol to reduce costs.

CONCLUSIONS

Several viable options are available for *in situ* treatment of Cr6. The selection of a Cr6 treatment alternative will be contingent on factors including depth of treatment, accessibility, and intended use of the aquifer. Potential production of treatment by-products such as arsenic and manganese may play an important role in the selection process.

REFERENCES

- Wilkin, R.T., Su, C., Ford, R.G., and Paul, C.J. (2005). Chromium removal processes during groundwater remediation by a zerovalent iron permeable reactive barrier. *Environ. Sci. Technol.* 39:4599-4605.
- Szecsody, J.E.; Fruchter, J.S.; Williams, M.D.; Vermeul, V.R.; Sklarew, D. (2004) In situ chemical reduction of aquifer sediments: Enhancement of reactive iron phases and TCE dechlorination. *Environ. Sci. Technol.* 38:4656-4663.
- Ludwig R., C. Su, T. R. Lee, R.T. Wilkin, S.D. Acree, R.R. Ross, A. Keeley (2007) In Situ Chemical Reduction of Cr(VI) in Groundwater Using a Combination of Ferrous Sulfate and Sodium Dithionite. *Environ. Sci. Technol.* 41:5299-5305.

GROUNDWATER ARSENIC TREATMENT USING PERMEABLE REACTIVE BARRIERS: AN OVERVIEW FROM FIELD AND LABORATORY TESTING

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INTRODUCTION

The major forms of arsenic in groundwater and surface water are the inorganic species arsenate [As(V)] and arsenite [As(III)]. The more oxidized As(V) species exist as oxyanions (H_2AsO_4^- and HAsO_4^{2-}) at near-neutral pH, whereas the primary As(III) species remains fully protonated as H_3AsO_3^0 at pH below about 9.2. Elevated levels of arsenate/arsenite in groundwater can be attributable to both natural and anthropogenic sources, including geologic sources, industrial wastes, agricultural pesticides, wood preservatives, and mine drainage. Lackovic et al. (2000) concluded that zerovalent iron could be used in permeable reactive barriers (PRBs) to remove inorganic forms of arsenic from groundwater, including arsenate and arsenite. These researchers noted that the removal mechanism for arsenic contrasted with that of chlorinated hydrocarbons (reductive chlorination) and hexavalent chromium (reductive precipitation), and involved either adsorption or precipitation on the iron surface. In general, the ratio of lab-based to field-based studies of arsenic removal using passive techniques is high, with the later being necessary to refine approaches and to evaluate realistic expectations for remediation at waste sites. In this presentation, findings from both laboratory studies and field studies will be presented and compared.

REACTIVE MEDIA AND ARSENIC UPTAKE PROCESSES

Since the Lackovic et al. (2000) paper there has been a considerable research effort focused on zerovalent iron and its potential for removing arsenic from water (e.g., see references in Wilkin et al., 2009). In addition, testing has been conducted on mixtures of zerovalent iron with other media such as organic compost (e.g., Ludwig et al., 2009; Gibert et al., 2010) and basic oxygen furnace slag (BOFS; Ahn et al., 2003). A common finding of these studies is that arsenic removal from water is attributable to adsorption onto corrosion products of zerovalent iron, including iron hydroxides, oxyhydroxides, and mixed valence Fe(II)-Fe(III) green rusts. Other studies have indicated that arsenic removal processes in zerovalent iron are linked to interactions with sulfur (e.g., Köber et al., 2005; Beak and Wilkin, 2009). Understanding the mechanism of arsenic uptake in the reactive medium is significant, because the mechanism can provide insight into long-term capacity estimates and reversibility assessments. The key uptake mechanisms, characterization approaches, and significance for sustainable remediation will be reviewed in the talk.

RESULTS OF FIELD TESTING

Pilot-scale subsurface installations of reactive media have been constructed at the East Helena Superfund Site (Montana, USA; Wilkin et al., 2009) and at a former phosphate fertilizer manufacturer (South Carolina, USA; Ludwig et al., 2009).

The East Helena PRB was installed in June 2005. It is 7 m long, 14 m deep, and 1.8 to 2.4 m wide (in the direction of ground-water flow). The reactive barrier was designed to treat groundwater contaminated with moderately high concentrations of both arsenite and arsenate at a former metal smelting facility. Monitoring results indicate arsenic concentrations >25 mg/L in wells located hydraulically upgradient of the PRB. Within the PRB, arsenic concentrations are reduced to 1,500 to <10 µg/L.

The demonstration pilot PRB in Charleston, South Carolina is about 7.9 m in length, 4.1 m deep, and 1.8 m wide (in the direction of groundwater flow). Performance monitoring showed that influent arsenic concentrations as high as 206 mg/L were treated down to average concentrations of <30 µg/L within the PRB (Ludwig et al., 2009).

An update of performance results from the East Helena PRB will be provided along with the results of advanced spectroscopy measurements made on core materials collected from both sites.

CONCLUSIONS

General conclusions and observations can be made regarding the application of PRB technology with granular iron for treatment of arsenic in groundwater.

- Zerovalent iron (alone or in mixtures) can be effectively used to treat groundwater contaminated with arsenic given appropriate geochemical and hydrological conditions.
- Arsenic removal processes appear to be complex as multiple bonding and coordination environments around arsenic are revealed using advanced spectroscopic techniques. Sequestration mechanisms taking place in the field are more varied compared to those indicated in highly controlled laboratory tests.
- Granular iron has a finite capacity to remove arsenic from solution. Successful applications of PRB technology for arsenic removal require detailed subsurface characterization data that capture geochemical and hydrogeologic variability. Evaluation of depth-dependent arsenic flux is critical. Zones with maximal contaminant flux will necessarily dictate system design requirements.
- Sodium-sulfate-type groundwater is better suited for contaminant treatment by zerovalent iron over calcium-bicarbonate-type groundwater. Carbonate precipitation is an undesirable consequence of zerovalent iron applications and is expected to reduce long-term reactive and hydraulic performance. Microbial reduction of sulfate to sulfide and precipitation of low-density iron sulfides within the reactive medium creates additional mineral surfaces for arsenic removal.
- Source control measures will reduce arsenic loading to the PRB and implementation of such measures should result in increased PRB lifetimes. The increase in effective lifetime should be directly proportional to the level of concentration reduction achieved by isolating and/or treating the source of contamination.

REFERENCES

- Ahn, S.A., Chon, C.-M., Moon, H.-S., and Kim, K.-W. (2003) Arsenic removal using steel manufacturing byproducts as permeable reactive materials in mine tailing containment systems. *Water Research* 37: 2478-2488.
- Beak, D.G. and Wilkin, R.T. (2009) Performance of a zerovalent iron reactive barrier for the treatment of arsenic in groundwater: Part 2. Geochemical modeling and solid phase studies. *Journal of Contaminant Hydrology* 106: 15-28.
- Köber, R., Welter, E., Ebert, M., and Dahmke, A. (2005). Removal of arsenic from groundwater by zerovalent iron and the role of sulfide. *Environmental Science and Technology* 39: 8038-8044.
- Gibert, O., de Pablo, J., Cortina, J.L., and Ayora, C. (2010) In situ removal of arsenic from groundwater by using permeable reactive barriers of inorganic matter/limestone/zero-valent iron mixtures. *Environmental Geochemistry and Health* 32: 373-378.
- Lackovic, J. A., Nikolaidis, N. P., and Dobbs, G. M. (2000) Inorganic arsenic removal by zero-valent iron. *Environmental Engineering Science* 17: 29-39.
- Ludwig, R.D., Smyth, D.J.A., Blowes, D.W., Spink, L.E., Wilkin, R.T., Jewett, D.G., and Weisener, C.J. (2009) Treatment of arsenic, heavy metals, and acidity using a mixed ZVI-compost PRB. *Environmental Science and Technology* 43: 1970-1976.
- Wilkin, R.T., Acree, S.D., Ross, R.R., Beak, D.G., and Lee, T.R. (2009) Performance of a zerovalent iron reactive barrier for the treatment of arsenic in groundwater: Part 1. Hydrogeochemical studies. *Journal of Contaminant Hydrology* 106: 1-14.

REACTIVE (OXYGEN) GAS BARRIER AND ZONE TECHNOLOGY

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INTRODUCTION

This work is an overview about Germany's best practice in gas PRB engineering. After a decade of scientific investigation and field scale testing, reactive gas barriers and zones (RGBZ or gas PRB's) are now introduced as a state-of-the-art technology for remediation of both organic and inorganic contaminations in the groundwater zone.

RGBZ technology is a sustainable green technology that is used to achieve long term and stable attenuation of negative impacts on groundwater bodies and flow. It requires moderate investment and operational costs and consumes low budgets of resources (e.g. energy, materials, land use, manpower). It is also characterized by low levels of operational risks and risks to human health or environmental fate. The RGBZ technology has demonstrated a high efficiency in stimulating the intended transformation and exchange processes while at the same time showing a low sensitivity to temporal changing geohydraulic and geobiochemical conditions. Variants of RGBZ can be implemented as stand-alone technologies, but they are also suitable for treatment train applications to deal with complex contaminations. Presently, RGBZ is approved by German environmental authorities and more applications are upcoming with regard to enhanced natural attenuation (ENA).

CONDITIONS AND AREA OF APPLICATION

While for solid phase (e.g. Fe⁰, activated charcoal) and liquid phase PRB's, engineered constructions of permeable gates or trenches and funnelling elements are necessary, all instrumentations for gas PRB's can be installed with minor effort. Only a few small diameter vertical perforations are needed, and coupled reactive zones can be formed in undisturbed geologic structures. This way, invasive effects on groundwater flow are minimized and RGBZ works as a real passive technology. Injection and transportation of a gaseous mixphase in the subsurface is performed in partially controllable 3-dimensional gas flow networks which can be used permanently or by multiple pulsing. Reactants are temporarily stored in the porous matrix in trapped gas clusters, adjacent to sorbed contaminants and biofilms bringing all them into contact with groundwater migrants. The delivery of gaseous reactants to groundwater flow can be controlled by partial pressure values.

RGBZ is strongly dependent on the hydrogeological domain. Because gases are used as reactive substances, it is additionally dependent on the pneumatic or gas flow characteristics of the subsurface. Thus, it is necessary to understand and manage a complex heterogeneous multi-phase, multi-component flow and migration domain.

Besides the suitability of the geological domain with regard to the installation of technical equipment and the performance of gas injections, restrictions can occur due to type and complexity of the limiting reactants and their ability to be transported by gas flow. Furthermore, the availability of sufficient time and space conditions to achieve given protection or remediation goals can limit the application of RGBZ. Most research is done and practical experience is gained using air and pure oxygen gas to supply accessible electron acceptors for aerobic biodegradation processes of organic and inorganic contaminants. Also the main demand exists for these reactants. Presented application examples therefore focus on oxygen gas PRB's. Noble gases like helium, argon and neon, but also SF₆ are used for gas tracing. Electron donor supply by methane and hydrogen gas injection is studied for stimulation of anaerobic degradation (e.g. for CHC or sulphate reduction). In situ iron removal from groundwater can be achieved by precipitation through oxygen and ammonia gas applications.

ENGINEERING

First, an overview is given about research contributions to theory, modelling and testing of gas-water flow and thermodynamics in the groundwater environment. For example, coherent gas channelling and pervasive bubbly gas flow, dynamic and residual (trapped) gas storage and their permeability implications were studied at pore to pilot scales as well as kinetic multi-component mass transfer at gas-water interfaces, particle transport capability of moving interfaces and degassing and gas clogging. The contributions are evaluated by means of importance for field application of RGBZ technology.

Best practice techniques for site investigation and technology installation are presented. Drilling and direct push methods like CPT, hammering (e.g. geoprobe[®]) and the new Sonic[®] vibration drilling are compared, taking into account soil type and compaction influence on perforation depths, multilevel installation capabilities, and sealing needs to avoid preferential gas escape. A complete technical set-up is given for RGBZ installations including gas injection lances, monitoring elements and sampling techniques for degassing sensitive groundwater, and e-sensing arrays for the redox and multiphase hydraulic state control. The importance of integral site testing methods like gas tracing, immission pumping tests and gas storage tests is discussed for dealing with heterogeneity-caused uncertainties.

After that, the main technical (engineering) planning steps for an RGBZ field application are reflected on. During a pre-selection step, restrictions are evaluated by means of treatment domain and goals, techniques and their alternatives, safety and acceptance risks. Detailed field scale gas-hydrogeological, biogeochemical and contamination surveying is followed by a pre-dimensioning step. Multiphase flow and main transformation processes need to be identified, parametrized and balanced using adequate modelling and lab testing methods. Completing the estimation of reactive zone space and time scales, the technical design of the field equipment including automation is elaborated on.

APPLICATION EXAMPLES

Examples are presented for applications of oxygen gas PRB's in sediment (1-3) and bedrock (4) environments. These examples share the experiences gained in performance and monitoring of gas-water-hydraulics, formation and control of coupled reactive zones, including homogenization aspects and phase transfer processes like precipitation, and integrated model based evaluations with prognosis of long term effects.

- 1) Transformation of an ammonium plume to clean up a subsurface drinking water reservoir and to protect a drinking water well field.
- 2) Enhancing biodegradation of organic (aliphates, BTEX, PAK, phenols) plumes at former lignite processing works.
- 3) Protection of a river stream from organic (short chained aliphates, BTEX) pollution originating from a petrol storage site.
- 4) Attenuation of leaching DOC and ammonium at a former unsealed urban deposit.

REFERENCES

- Engelmann, F.I., Ehbrecht, H., Giese, R. and Roscher, C (2003): Technologies and formation of permeable reactive barriers in aquifers using direct injection of reactive gases. Proceedings DGFZ, ISSN 1430-0176. N° 24, pp. 101-125 (in german).
- Engelmann, F.I. and Hüttmann, S. (2009): Development of a gas measurement system and an injection technology for high-pressure pulsed gas injection and for a controlled performance of subsurface gas storage zones. Technical report KF0011010SB7 to the German Ministry of Economy (in german).
- Uhlig, U., Kassahun, A., Luckner, L. and Zschiedrich, K. (2008): Pilot test of an active drain & gate system in a multi-step reactive barrier. Proceedings ConSoil2008, ISBN 978-3-00-024598-5, pp.360-363.

EFFECTIVE CLEANUP OF GROUNDWATER CONTAMINATED WITH URANIUM USING PERMEABLE REACTIVE BARRIERS

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INTRODUCTION

Mining of natural resources always causes environmental impact such as land use, large quantities of waste, destruction of habitat, impairment of groundwater regime, and quite possibly contamination of soil, water or air (Dudka and Adriano 1997). Uranium contamination in groundwater resulting from uranium mining and processing occurs worldwide at numerous locations. In view of its toxicity rather than radioactivity, a limiting concentration of 0.015 to 0.030 mg/l is currently being considered (Giddings and Fawell 2004).

Permeable reactive barriers (PRBs) offer an alternative as opposed to more cost-intensive active methods for groundwater remediation, e.g. pump-and-treat. Long-term performance of PRBs, however, is crucial for the technology's success. Good removal results have been achieved using elemental iron with possible reaction paths being reductive precipitation and adsorption on to corrosion products of Fe⁰.

Uranium can also be removed by dissolution of HAP and subsequent precipitation of low-solubility uranyl phosphates such as autunite Ca(UO₂)₂(PO₄)₂ or chernikovite H₂(UO₂)₂(PO₄)₂. Other possible reaction mechanisms for uranium removal with HAP are ion exchange processes and surface sorption with HAP (on two possible surface groups).

At the former uranium mining site in Pécs (Hungary) a pilot PRB system with elemental iron as reactive material was installed. Results from operation are reported.

METHODS

In the lab experiments elemental iron was used in concentrations between 5 and 70 % in sand. The concentration of HAP was between 10 and 20 %. Uranium concentrations used were 0.5 and 9.6 mg/l U, respectively. A more detailed description of the experimental set-up can be found elsewhere (Biermann et al. 2005).

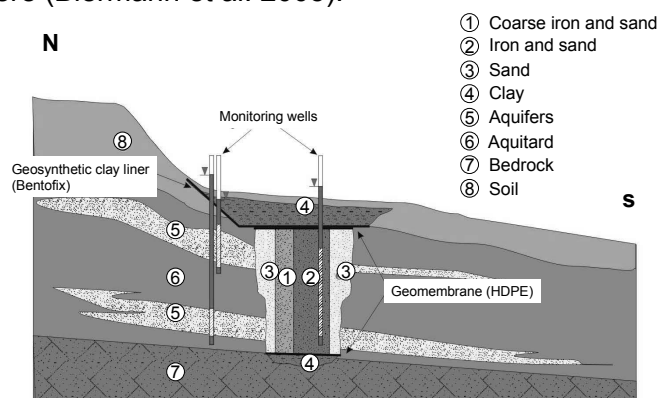


Figure 1. Sketch of the design of the PRB field test installation near Pécs.

The PRB in the field experiment consists of two different zones, zone I with a lower content of coarse elemental iron (12 % by volume or 0.39 t/m³, grain size 1 – 3 mm) and zone II with a higher content of fine elemental iron (41 % by volume or 1.28 t/m³, grain size 0.2-3 mm).

On both sides (upstream and downstream) sand layers were inserted to distribute water inflow and outflow. The PRB is sealed with clay and geosynthetic clay liners at the bottom and with a geomembrane (high density polyethylene) at both sides and on the top. The design is displayed in Figure 1. The total mass of elemental iron installed as reactive material was 38 t, from which 5 t was coarser material.

RESULTS AND DISCUSSION

In the lab column experiments Fe^0 and HAP exhibited a uranium retention of more than 99 %. Effluent uranium concentrations were below the limit of detection of the spectrophotometric method employed for routine uranium analysis. Measurements with ICP-MS yielded maximum effluent uranium concentrations of 1.3 $\mu\text{g/l}$ corresponding to a uranium retention of at least 99.7 % for all columns. In the experiment with 9.6 mg/l U, a breakthrough occurred in the HAP-column with effluent uranium concentrations exceeding the proposed limit of 15 $\mu\text{g/l}$ in drinking water (Giddings and Fawell 2004) after the treatment of 3.2 l of artificial groundwater (AGW). Up to this point, however, more than 30000 mg U/kg HAP had been retained in the column. After the average uranium load had reached 50000 mg U/kg HAP the column was operated with AGW with no uranium to test for reversibility of the pollutant removal. Desorption was indeed observed, however, uranium concentrations in the effluent decreased with time. It is assumed that most of the uranium removed will be stable against remobilisation.

In the field test good removal results for uranium (99 %) were obtained since start of operation in 2002. Table 1 lists average values for different parameters for the operation period. It can be seen that the pH increases in the PRB by almost 2 pH units and that calcium is almost completely removed and precipitated.

Table 1. Monitoring data of the PRB as of March 22nd 2005 after 31 months of operation.

Well	Location	pH	EC $\mu\text{S/cm}$	U(VI) $\mu\text{g/l}$	TDS mg/l	Ca mg/l	SO_4 mg/l	HCO_3 mg/l	Fe mg/l
PRB-1	Inflow	6.9	1400	940	1010	150	320	525	0.002
PRB-10	Zone I	7.3	1330	37	937	125	300	275	5.5
PRB-11	Zone II	8.7	865	10	550	10	185	299	0.03
PRB-14	Outflow	8.7	780	2	540	14	170	268	0.03
PRB-3 ^a	Downstream	8.5	420	56	240	5	95	116	0.017

^a Water is probably diluted by lateral water flow

CONCLUSIONS

Elemental iron and HAP can be used as reactive material in PRBs to remove uranium from groundwater. In the case of iron the formed precipitates might have an influence on the long-term performance of the installation due to the risk of clogging. Long-term stability of sorption complexes or mineral phases is essential for PRB systems using HAP for uranium removal. Evidence exists that under common groundwater conditions uranium remains immobile (Giammar 2001).

REFERENCES

- Biermann, V., Simon, F.G., Csövári, M., Csicsák, J., Földing, G. and Simoncsics, G. (2005), Long-term performance of reactive materials in PRBs for uranium remediation, in: Merkel, B.J. and Hasche-Berger, A. (eds.), Uranium in the environment - mining impact and consequences, 275-285, Springer, Berlin
- Dudka, S. and Adriano, D.C. (1997), Environmental Impacts of Metal Ore Mining and Processing: A Review. *Journal of Environmental Quality* 26, 590-602
- Giammar, D. (2001), Geochemistry of uranium at mineral-water interfaces: rates of sorption-desorption and dissolution-precipitation reaction. California Institute of Technology, Ph. D. Thesis, Pasadena, CA, USA
- Giddings, M. and Fawell, J. (2004), Uranium in Drinking-water, Background document for the development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/11

CHOOSING THE BEST DESIGN AND CONSTRUCTION TECHNOLOGIES FOR PERMEABLE REACTIVE BARRIERS

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INTRODUCTION

Permeable reactive barriers (PRBs) and pump-and-treat are the two main field scale groundwater (GW) remediation technologies currently in widespread use. Since its introduction in early 1990, zero valent iron (ZVI) based permeable reactive barriers have become very popular for remediating groundwater contaminated by chlorinated hydrocarbons (Gavasker 1999). Currently about 160 ZVI-based PRBs are in operation around the world. Based on the past 20 years of pilot as well as field remediation experience, the design and construction of these barriers are identified as two of the most important parameters to meet the remediation objective in the short as well as long term. Selecting the best design and construction technologies also significantly helps to reduce the capital cost of the project and makes construction easier.

PRB DESIGN

PRBs form a barrier to contaminants, but not to groundwater. This form of passive treatment is intended to last throughout the life of the contaminated GW plume and remediate the target contaminant and its byproducts into innocuous substances. Due to the inherent lower flow rate of groundwater, a contaminated plume may last for many years, even for decades. As the plume changes with time, the contaminant concentration reaching the reactive barrier also varies. The physical and chemical parameters of GW as well as its flow rate and level in the aquifer also vary. Once a reactive barrier is installed, there is very little possibility of carrying out active maintenance. This means the barrier design needs to take account of all the variables and ensure consistent performance throughout its entire life span in order to meet the remedial objectives of the site. The three main types of PRB now in use are continuous barrier, funnel & gates (F & G) and reactive vessels (Mckenna et al.2011). For successful implementation of a PRB, extensive characterization of the site, the groundwater and the plume is vital. The key to effective design selection lies in the available technology, its affordability and the contractors' expertise. The laboratory batch study method is the fastest and easiest screening tool for selecting a suitable reactive material as well as for understanding the kinetics of the contaminant and its byproducts, using samples from the particular site. The best reactive material identified in the batch study can then be used to conduct the long term column study, which employs site GW under similar flow conditions to those of the site itself. To obtain meaningful data from a column study, it should be conducted over several years. The kinetic data obtained from the column study is then used to calculate the size and volume of the reactive barrier. Possible failure conditions of the barrier will also be addressed in the design in order to avoid them as well as to ensure consistent performance over time. In the past 20 years, many column studies have been carried out using site GW and the established parameters are now available as data. Since a column study is a long term and costly commitment, provided the site GW parameters match those in the established data, then the need for a full column study may be minimised or even avoided. Identifying the concentration profile of the contaminant with GW flow throughout the site is essential to placing a suitable barrier at the optimum location, so as to minimize both the amount of reactive material used as well as construction costs. In this context, modeling and simulation play a vital role. All barriers are installed vertical to the GW flow direction. If the GW flow and plume geometry are well understood and there are no

other construction constraints, a continuous barrier is usually the design of the choice (Gavasker 1999). Continuous PRBs do not need to be built upon a low permeability zone as they will not divert groundwater downwards. Since the continuous reactive barrier captures the complete plume width, it generally requires a much larger amount of reactive material compared to the F & G design and the prevailing reactive material price then becomes a factor in choosing the most suitable design. Most field installations globally use the continuous reactive barrier system. The F & G PRB consists of an impermeable funnel and a very high permeable reactive gate (Birke et al. 2003). The funnel directs the GW towards the gates. To capture a wide plume width well, several funnels with gates may need to be installed. For extremely larger contaminant plumes or highly heterogeneous aquifers, the F & G system can be modified to contain multiple reactive zones. Since F & G alters the groundwater flow, the impermeable funnel needs to be firmly based on the impermeable aquitard. Even though the reactive material cost is low compared to a continuous barrier the impermeable barrier construction cost is much higher for the F & G. The joint between the permeable and impermeable barrier needs to be well sealed. The third sort of PRB, the Reactive Vessel is very similar to the F & G barrier except it replaces the gate with an in situ reactive vessel.

PRB CONSTRUCTIONS

PRB construction can be divided into reactive barrier construction and non reactive barrier construction. Both excavation and injection methods can be used for barrier construction (Day et al. 1999). The depth of the aquifer below the ground surface and soil conditions will determine the most suitable construction technique for the site, along with the contractors' expertise. Spoil generation as well as available space for construction are among key factors influencing the choice of construction technique. Biopolymer trenching, continuous trenching, unsupported excavation, supported excavation, and caisson excavation are among the main existing excavation techniques. Hydraulic fracturing, jetting and soil mixing are the main injection methods in PRB design. These costlier injection methods are more suited to higher depth PRB installations. Quality control in the reactive material handling, including filling and qualification (eg removal of biopolymer etc), confirming the compatibility of the slurry wall to the GW, slurry preparation, slurry wall construction and sealing of the reactive and non-reactive barrier gaps are all critical to good PRB design and construction. Equipment generally used to build a PRB includes backhoes, clamshells, continuous trenchers, vibratory hammers, soil mixers and jetting machines.

CONCLUSION

The past 20 years of data shows that if a PRB is designed and installed well, it will give consistent performance over a long time. Inorganic precipitation (and hence choking the barrier) is a one of the major issues to be overcome. Poor capture of the plume is another detriment to performance. The barrier design needs to factor in the corrosion rate of iron and hence the overall life of the barrier under the field GW conditions. Establishing the ZVI quality parameters and choosing the right grade is essential to preventing failure of the barrier due to use of the wrong ZVI quality. It is also advisable to consider the technical and cost alternatives available to meet the remediation objective in case a PRB failure occurs either in the short or long term.

REFERENCES

- Gavaskar, A.R. (1999) Design and construction techniques for permeable reactive barriers, *Journal of Hazardous Materials* 68: 41-71.
- Mckenna, A., Perlmutter, M., Williamson, D. (2011) Guideline document practical guidance on permeable reactive barriers, CRC CARE guideline document.
- Birke, V., Burmeier, H., Rosenau, D. (2003) Design, construction, and operation of tailored permeable reactive barriers, *Practice periodical of Hazardous, toxic, and radioactive waste management* 264-280.
- Day, S.R., O'Hannesin, S.F., Marsden, L. (1999) Geotechnical techniques for the construction of reactive barriers, *Journal of Hazardous Materials* B67: 285-297.

THE HISTORY OF AUSTRALIA'S FIRST REACTIVE IRON BARRIER

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INTRODUCTION

Containment and remediation of chlorinated hydrocarbons (CHCs) in groundwater is a challenging and often expensive undertaking. Traditional methods usually involve significant capital investment and ongoing operational costs. Resultant energy consumption and waste disposal requirements may also negate overall environmental benefits. However reactive iron barriers can eliminate many of the operating and maintenance costs associated with the traditional methods, even in complex groundwater conditions. It has also been found that the mode by which they degrade the CHCs can evolve with time, depending on the hydrogeochemistry of the groundwater system in which they are installed.

Since the installation of the first field scale trial of a reactive iron barrier (RIB) in 1994, granular zero valent iron (ZVI) has been employed in many contaminated sites around the world to degrade a wide range of volatile CHCs in groundwater. In February 1999, Orica Australia Pty Ltd installed the first pilot scale reactive iron barrier in Australia to evaluate the effectiveness of ZVI in destroying dissolved-phase CHCs. The selected test site is located downgradient of two former chlorinated solvent plants that operated for nearly forty years up until the early 1990s. Zones of dense non-aqueous phase liquid (DNAPL) had been detected in the subsurface, containing tetrachloroethene (PCE), trichloroethene (TCE) and carbon tetrachloride (CTC) as well as a range of intermediary and daughter products. Aggregate influent CHC concentrations ranged up to 220 mg/L.

Apart from the wide array of chlorinated hydrocarbons in the groundwater and their relatively high concentrations, the treatment zone differentiated itself from other sites where reactive iron barriers had been used with its complex hydrogeochemistry. In particular, the effects of high natural dissolved organic carbon (DOC) and low pH – as are present at the test site – had not been extensively studied elsewhere.

RESULTS AND DISCUSSION

Following 13 months of performance monitoring, a large amount of data has been amassed (Stening et al., 2000). The data was assessed to evaluate the effect of the site's high influent concentrations of chlorinated solvents and DOC on the reductive dechlorination reaction kinetics. Reaction half lives generally appeared to be higher than those published for other sites. This was thought to be a result of the relatively high DOC arising from the site's historic swampy conditions. However the overall average chlorinated solvent mass reduction was approximately 78%, which satisfied the pilot scale objectives. Temporal trends were evident, but these were not consistent with increasing depth or DOC. Another factor that reduced apparent mass reduction was the presence of 1,2-dichloroethane (1,2-DCA) and dichloromethane (DCM), which are known not to be degraded by the ZVI.

This pilot scale evaluation had demonstrated that ZVI could be used successfully to degrade a broad range of dissolved CHCs in a geochemically complex aquifer. As a result, Orica began planning the installation of a full scale RIB, up to 300 m long, 0.4 m thick and 20 m deep. At that time, though, no suitable technology could be found to reliably and predictably emplace such a large RIB in flowing sands of the Botany Aquifer. Furthermore, regulatory action necessitated the installation of a large hydraulic containment and ex situ treatment ('pump and treat') system, which in effect effectively made the RIB a redundant remediation measure.

Additional periodic monitoring has been conducted to evaluate the pilot-scale RIB's long-term performance (Stening et al., 2008). Results in May 2002 (month 39) showed signs of 1,2-

DCA dechlorination. Sampling in November 2006 (month 91) confirmed this. Groundwater conditions have changed markedly in the test site, largely due to the pump and treat system altering plume flow directions. Consequently, with the exception of 1,2-DCA, aggregate CHC concentrations into the RIB have decreased to less than 60 mg/L; 1,2-DCA concentrations have risen to as much as 127 mg/L. Reaction rates have decreased little with time, and gradual fouling is not yet enough to impair RIB hydraulics. Most notably, though, 1,2-DCA is now being removed in the RIB – by up to one or two orders of magnitude. The cause of the 1,2-DCA mass removal has been found to be due to microbial colonisation of the barrier by dehalorespiring and/or hydrogen utilising bacteria, including *Dehalococcoides* and *Dehalobacter* (Stening et al., 2008). Although this phenomenon has been observed at the laboratory scale for other compounds, this appears to be the first reported instance of this in the field for 1,2-DCA.

CONCLUSIONS

At the time of the installation of the first reactive iron barrier in Australia in February 1999 it was not certain whether it would be able to successfully degrade elevated concentrations of volatile chlorinated hydrocarbons in a low-pH, high-DOC aquifer. Nor was it envisaged that the hydrogeochemical conditions would be dramatically altered due to the subsequent installation and operation of a large hydraulic containment system. Yet through these periods the RIB was able to achieve significant contaminant mass reduction, and the mode of degradation evolved from abiotic to biological reductive dechlorination. Exploiting the phenomenon of microbial colonisation might broaden the capability of RIBs to treat in situ hitherto recalcitrant dissolved phase compounds.

REFERENCES

- Stening, J.R., Vogan, J., and Duran, J.M. (2000) Assessment of Reactive Iron Barrier Performance at a Complex Australian Site. In: Johnston, C.D. (Ed.), *2000 Contaminated Site Remediation Conference, from source zones to ecosystems*. Centre for Groundwater Studies, CSIRO Land and Water, Wembley, WA.
- Stening, J.R., Manefield, M., Lee, M., Low, A., Zemb, O., Przepiora, A. and Vogan, J. (2008) Reductive Dechlorination of 1,2-Dichloroethane in a Reactive Iron Barrier. In: *Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. 19-22 May 2008, Monterey, California. Battelle.

GROUNDWATER MODELLING USING PRBs — GENERAL ASPECTS, CASE STUDIES

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INTRODUCTION

Permeable Reactive Barrier (PRB) technology is increasingly becoming a viable option for remediating contaminated ground water. Modelling of subsurface hydrogeology is implemented at various stages of the PRB technology. The general aspects of PRB design and implementation was discussed in detail by Gavaskar (1998). There are two basic designs of PRBs commonly used: funnel and gate and continuous trench barriers (Mc Mohan et. al., 1999). The stages of PRB technology include the initial feasibility assessment, laboratory treatability studies including the column studies, estimation of PRB design parameters and developing a long-term monitoring network for the performance evaluation of the barrier. This paper presents an overview of mathematical models used for implementing the PRB technologies.

DISCUSSION

Numerical and analytical models are commonly utilized in modelling the various stages of designing PRBs. Generally building a simulation model for a PRB is site specific and recent advances in understanding the various transport and hydrogeochemical processes will enable us arrive at a reliable predictive model. A case study of PRB modelling in South Australia is discussed in this study. The site is contaminated with TCE and extensive site investigations demonstrate the high degree of subsurface heterogeneity. Modelling at this study area considers the combination of active and passive remediation technology to manage TCE contamination. Active remediation is applied to manage the contamination at source region and passive remediation technology, PRB is applied at the tip of the plume such that the remediation is taking place under controlled hydraulic conditions. Passive remediation by the REMAT™, reactive filtration material filled annular space of the extraction wells was evaluated in the model. Here, the groundwater is remediated while it passes through the annular space of the extraction wells by the adsorption of TCE on the REMAT™. As the hydraulic conditions of the reactive material are better than those in the sediments, the sphere of influence of the passive wells is slightly bigger than their large diameter. The numeric simulations were carried out for duration of 30 years.

METHODS

The PRB modelling calculations were carried out for the case study using the Feflow FM3D software, Version 5.4 by DHI-WASY GmbH, Germany. It is finite element software for the simulation of groundwater flow and reactive transport. Principally, two distinct groundwater flow and transport models were set up: one displays the whole active remediation process (model I) and the second (model II) calculates the passive impact of the extraction wells at the tip of the plume, once the active remediation is stopped. The area of the regional model (model I) has a dimension 2.36 km² and 219,648 spatial elements. The area of site 9 covers only 0.176 km², but the spatial elements are much smaller here (about 10 m², high spatial discretisation). Model II has a number of 159,168 elements with a model surface area of 11,400 m². Here, the mean element size is 0.1 m² (min. 0.05 m², max. 1.125 m²)

CONCLUSION

General aspects of hydrogeological modelling for PRBs and overview of existing models are discussed. The modelling applied for the case study discussed in the paper demonstrate that by infiltrating cleaned groundwater at the fringe of the plume, the gradient is also increased. The simulations, however, show that an extensive increase of the hydraulic gradient is only achieved with a great number of extraction/injection wells, because even with the maximum pumping/injection rate the cone of depression/groundwater elevation of each well covers only a very small zone. If, on the other hand, the extraction wells are positioned with only a little distance to each other, the cones of depression form a connected drawdown which enhances the remediation significantly. The evenly distributed infiltration wells at the fringe of the plume have only little influence on the hydraulics.

REFERENCES

- Gavaskar A.R, Gupta, N Sass B.M, Janosy R.J., O'Sullivan D. 1998. Permeable Barriers for Groundwater Remediation: Design, Construction, and Monitoring, Battelle Press, Columbus, OH.
- McMahon PB, Dennehy KF, Sandstrom MW. 1999. Hydraulic and geochemical performance of a permeable reactive barrier containing zero-valent iron, Denver Federal Center. Groundwater 37(3): 396–404.

COMPARATIVE PERFORMANCE OF TWO REACTIVE MATERIALS IN REMOVING PETROLEUM HYDROCARBONS FROM CONTAMINATED GROUNDWATER IN WESTERN AUSTRALIA

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INTRODUCTION

Successful installation of a permeable reactive barrier (PRB) requires both stable and reactive material with the capacity to rapidly cleanup total petroleum hydrocarbons (TPH). The choice of reactive material depends on the nature of contaminants and the stability of the material constituting the reactive medium. Thus synthesis and testing of the reactive barrier materials is critical to the success of the remediation system.

Historical storage and use of petroleum hydrocarbons at the study site, a port facility located in Western Australia is impacting the underlying groundwater. Environmental studies conducted by various consultants have identified dissolved phase hydrocarbon (DPH) and light non aqueous phase liquid (LNAPL) plumes impacting the groundwater aquifer. A number of hotspots exist at the site notably confirmed by significantly elevated concentrations of TPH at groundwater monitoring wells.

Due to high hydraulic conductivity of the site, it has been inferred that the contaminated plume will have an impact on the nearby marine environment. CRC CARE conducted a study on the comparative performance of two reactive media for their use in the construction of a PRB, to remediate TPH contaminant and eliminating the associated risks to the environment.

METHODS

Two pre-selected reactive materials, ReMat, a proprietary material and granulated activated carbon (GAC), a sorbent material, packed in columns were tested for their suitability in a PRB. Column apparatus were specifically developed and designed in order to facilitate targeted sampling of the groundwater through the porous reactive material. Contaminated groundwater was collected from the site and used during the column tests. A groundwater flow rate of 3.0 mL/min, the worst case scenario, through the column was considered to simulate the highest potential groundwater velocity on the study site of approximately 500 meters per year.

The data obtained from reactive material investigations using column tests were used in designing the PRB to be constructed at the site. PRB was designed based-on the methodology suggested by Gavaskar *et al.* (1999).

The breakthrough point in the experiment was defined as the TPH detected at or above the Dutch Intervention Level (600 µg/L) in the column effluent as there is currently no health or ecological investigation level in Western Australia for total petroleum hydrocarbons in groundwater.

RESULTS AND DISCUSSION

TPH removal efficacy of ReMat (Figure 1) was found to be comparable to that of GAC, as efficiency of both reactive materials diminished in a similar trend over time.

ReMat removed 100% of TPH in the groundwater for 10 days and subsequently breakthrough commenced after 24 days. GAC removed 98-100 % of TPH in the contaminated groundwater for up to 19 days, however, breakthrough commenced after 28 days of operation. Through experimental data extrapolation, it was predicted that for both ReMat and GAC, exhaustion point would be reached within approximately 90 days of operation.

Incorporating the column tests data with Gavaskar et al (1999) methodology, the proposed PRB for the study site is 600m (length) x 1.15m (width) x 3m (depth). A total volume of 2,070 cubic meters of ReMat is required to construct the PRB with the potential to remediate approximately 3 tonnes of TPH contaminants from groundwater that has a high risk of impacting the marine ecosystem. However, the calculated PRB thickness for GAC will be 1.37m. Based on the cost benefit analysis undertaken by the authors, it was found that ReMat is half the cost of GAC.

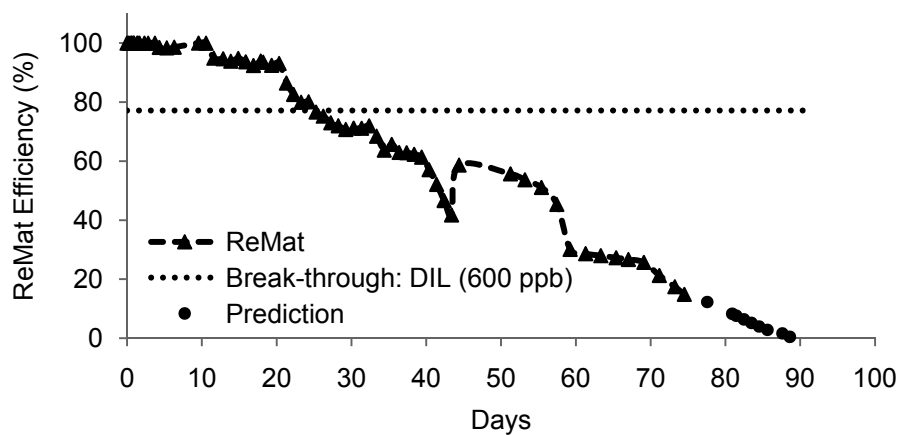


Figure 1. ReMat's efficiency in removing TPH from AW18 groundwater

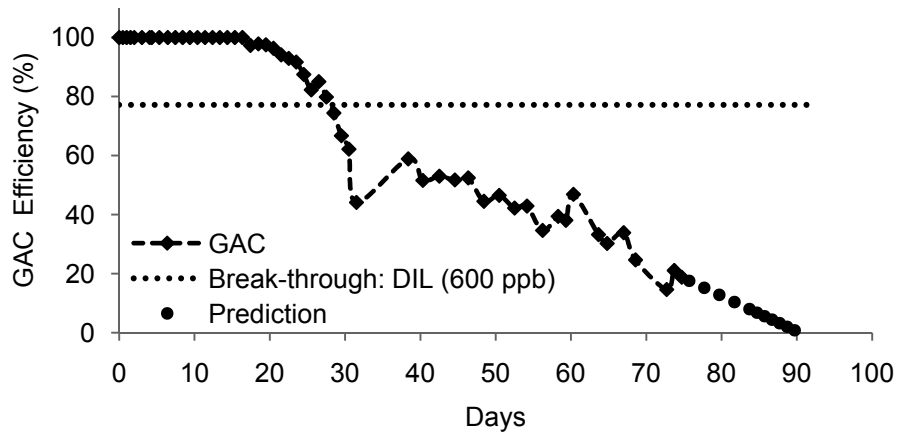


Figure 2. GAC's efficiency in removing TPH from AW18 groundwater.

CONCLUSIONS

The capacity of ReMat to remove TPH on a volume basis as determined by the column tests was slightly higher than that of GAC. Therefore, an inexpensive *in-situ* remediation technology such PRB with ReMat as its reactive material is suitable for eliminating the risks of TPH contamination to nearby marine environment.

REFERENCES

Gavaskar A. R. (1999). "Design and construction techniques for permeable reactive barriers", Journal of Hazardous Materials **68**: 41-71.

ELECTRONIC WASTE AND ITS MANAGEMENT IN DEVELOPING NATIONS

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Electronic waste (e-waste) is the fastest-growing stream of municipal solid waste and has been an emerging environmental health issue in both developed and developing countries because of its massive production volume and insufficient management policy in many countries (Ogunseitan et al. 2009). E-waste contains metals and persistent organic pollutants (POPs); inappropriate recycling processes occur in several developing countries and result in the release of these toxicants into the environment (LaDou and Lovegrove 2008). Although serious health concerns arise from these primitive recycling activities, the research needs are largely unaddressed. It is estimated that 20–50 million tons of e-waste are produced annually worldwide; the United States, Western Europe, China, Japan, and Australia are the major producers (Cobbing 2008; Davis and Herat 2010; Robinson 2009). Rapid obsolescence of electronics goods, compounded by dumping from developed countries, has brought the electronic waste (e-waste) problem in India to the brink of spilling over into an acute crisis. The current practices of e-waste management in India suffer from a number of drawbacks like the difficulty in inventorying, unhealthy conditions of informal recycling, inadequate legislation, poor awareness and reluctance on part of the corporate to address the critical issues. The present study highlights the associated issues and strategies to address this emerging problem, in the light of initiatives in India.

APPROACH AND METHODOLOGY

The two basic approaches applied for carrying out e-waste assessment in the India involved quantification of the available data and reports revealing the toxic effect related to e-waste recycling issues. E-waste processing involves primary dismantling of items from e-waste, e.g., the unscrewing of a PC monitor and removal of the cathode ray tube (CRT) and printed circuit boards. E-waste production/end products involve processes consisting of secondary dismantling of items obtained as output of e-waste processing, e.g., the re-gunning of CRTs, extraction of metals, and others. E-waste contains many toxics such as heavy metals, including lead, cadmium, mercury; Polychlorinated Biphenyls (PCBs), Poly Vinyl Chloride (PVC), etc, in some components.

RESULT AND DISCUSSION: MAGNITUDE OF E-WASTE PROBLEM IN INDIA

India is growing at an exponential rate in terms of electronic waste (e-waste), generating approximately 150,000 t/year and is mostly stockpiled or poorly managed. Mumbai produces 11,017 tons of e-waste annually. Delhi comes next with 9,730 tons of e-waste. Surprisingly, India's Silicon Valley, Bangalore, comes third, producing 4,648 tons. Next is Chennai with 4,132 tons and Kolkata with 4,025 tons. In India, it is estimated that the e-waste is 0.1-0.2% of the total municipal waste. In addition to this, about 1050 tons per year of computer waste comes from retailers and manufacturers. A recent report by Toxics Link (2004) found that 70% of electronic waste collected at recycling units in New Delhi (India) was actually exported or dumped by developed countries. Fig 1 shows the amount of e-waste generated in different nations between 1997 and 2009. In India, most of the recyclers currently engaged in recycling activities do not have this expensive technology to handle the waste. Recycling mass produced consumer products such as white goods, refrigerators, and washing machines, is not new, and sophisticated infrastructures for scrap metal have been in place for decades. However, electronic products are a major new category, which have experienced rapid growth over the last decade, particularly in the area of personal computers. The communities that are affected by the toxics in e-waste need not necessarily

be those that are creating the waste. The unethical export of e-waste by industrialized nations to developing countries is shifting the onus of development to communities ill-equipped to deal with such waste. A lot of these materials are being sent to developing nations under the guise of reuse in order to bridge the digital divide. Computer scrap is managed through various management alternatives such as product reuse, conventional disposal in landfills, incineration and recycling. However, the disposal and recycling of computer waste in the country has become a serious problem since the methods of disposal are very rudimentary and pose grave environmental and health hazards. In addition, besides handling its own computer waste, India now also has to manage the waste being dumped by other countries. A statistically significant ($p < 0.05$) positive linear correlation has been observed between the amount of e-waste generated in 2005 and the atmospheric concentration of PCBs in Bangalore, Chennai, New Delhi, Mumbai and Kolkata (Paromita Chakraborty, Dioxin 2010). PCB related to dumped waste in India is becoming more complicated by the invasion of e-waste, particularly computer waste. This projects the upcoming emission sources of this group of pollutants mostly from the urban locations apart from the toxic metals like mercury, lead and cadmium.

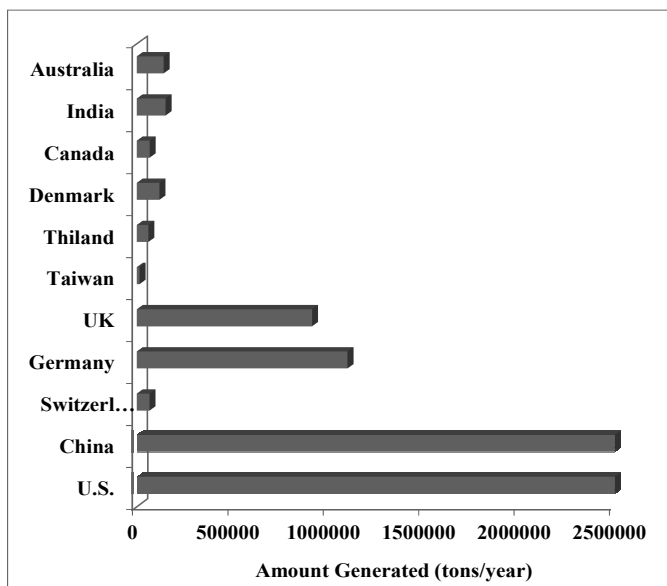


Fig 1. Amount of e-waste generated in different countries. between 1997-2009 (tons/yr)

CONCLUSION

E-waste is omnipresent. It is characterized by its unusual chemical composition and the difficulties associated with determining its mass and flux at both local and global scales. Contamination associated with E-waste has already caused considerable environmental degradation in poor countries and negatively affected the health of the people who live there.

REFERENCES

- Ogunseitun OA, Schoenung JM, Saphores JD, Shapiro AA. (2009). Science and Regulation. The electronics revolution: from e-wonderland to e-wasteland. *Science* 326:670–671.
- LaDou J, Lovegrove S. (2008). Export of electronics equipment waste. *Int J Occup Environ Health* 14:1– 10.
- Cobbing M 2008. Toxic Tech: Not in Our Backyard. Uncovering the Hidden Flows of E-Waste. Report from Greenpeace International, Amsterdam.
- Davis G, Herat S. 2010. Opportunities and constraints for developing a sustainable e-waste management system at local government level in Australia. *Waste Manag Res* 28:705–713.
- Toxics Link (2004): Is India becoming dumping ground for British e-waste? (<http://www.toxicslink.org/mediapr-view.php?pressrelnum=5>).
- Paromita Chakraborty, Gan Zhang, Paul K.S. Lam and Kevin C Jones; In Dioxin 20XX San Antonio 2010, USA. 30th International Symposium on Halogenated Persistent organic pollutants (POPs), September 12th-17th 2010. Polychlorinated biphenyls in the atmosphere of seven major Indian cities.

COMPARISON OF E-WASTE MANAGEMENT STRATEGIES BETWEEN DEVELOPED AND DEVELOPING COUNTRIES

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INTRODUCTION

Waste electrical and electronic equipment (WEEE) contains many hazardous materials requiring specialized disposal and recycling techniques. E-waste already equals 1% of developed countries' solid waste. Such countries as India and China have also witnessed E-waste become their fastest-growing waste source, some locally produced, some arriving from developed countries. In China, India, Pakistan and other less-developed countries, the facilities and trained professionals needed for safely handling and disposing of the growing E-waste range from inadequate to hardly existing. Much the same can be said for regulations dealing with this waste, and their enforcement. Nevertheless, a whole new economic sector in these countries is evolving around the trade, repair, recovery, and disposal of E-waste components. This goes on at great potential harm to the individuals involved and to the environment.

In the past two decades, the legal structures for dealing with E-waste and its consequences have been put in place in the developed world. These laws and policies seek to control environmental impacts from product manufacture, use and eventual disposal. The general guiding concept is known as extended producer responsibility (EPR), termed in international environmental law as the polluter pays principle (PPP).

REVIEW

Policies, Laws, Systems

The European Union and Japan have been leaders in formulating and then implementing E-waste regulations. In EU countries, the principle behind directives for collection, recovery and reuse has been extended producer responsibility, making producers responsible for the take-back of E-waste. Canada and Australia are among countries developing systems based on these principles. Japan has developed a system differing in some ways known as "Reuse, Recycling and Recovery" (UNEP, 2007).

E-waste management can be seen in terms of three elements: the national registry, the collection system and logistics. The national registry is primarily a list of producers and their collection obligations; the registry may be kept by a variety of agencies, which may also check compliance. Systems for E-waste collection are usefully grouped into two types. A *Collective System* is usually nonprofit and nongovernmental, and founded by trade associations, which concentrate on certain product categories for efficiency in finding markets for reuse. In the *Clearing House System*, producers, recyclers, waste businesses and such compete to provide services. The government sets the ground rules for allocation and monitoring, and provides the national registry to a coordinating body, from which that body may assign producer obligations; it also establishes waste collection points. E-waste collection logistics commonly involve three channels. Municipal collection sites usually accept any amount of waste from citizens, without cost. In-store retailer take-back schemes may be free or depend on repeat purchases. Producer take-back is generally for business customers and may require a replacement purchase.

Analyses of developed countries' E-waste management shows Japan to have perhaps the best-functioning system. Korea, Canada and Australia have well-advanced systems as well. Switzerland, Norway, Belgium, Sweden and the Netherlands have all exceeded minimum EU E-waste collection and recycling targets.

On the other hand, in countries including Argentina, Cambodia, China, India, Indonesia, Malaysia, Sri Lanka, and the Philippines, only local E-waste with a recycling value is collected, typically by scavengers working outside the guidance of regulations.

Initiatives

To address the large gap between developed and developing countries in handling E-waste, both physically and in the realm of policy, a variety of agencies have put forth initiatives.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal has been in place since 1992, with 164 signatories (the notable exception is the USA). This most comprehensive agreement charges producer countries with the safe disposal fates of exported products, while banning hazardous material exports to developing countries.

The 3Rs "Reduce, Reuse, Recycle" Initiative was introduced by Japan at a 2004 G8 Summit. Japan has promoted use of the 3Rs domestically and on the international stage. Among this initiative's goals are furthering the technologies of reuse, the cooperation of developed with developing countries on recycling and reuse programmes, and removing barriers to the international movement of materials for recycling and remanufacture (USEPA, 2007). This last objective has been seen by some as conflicting with tenets of the Basel Convention, which stress producer-nation responsibility.

StEP (Solving the E-waste Problem) is a UN-led initiative, organized in 2004, to enhance and coordinate various efforts around the world on the reverse supply chain. Its five categories of concentration are policy, redesign, reuse, recycling and capacity building.

The Basel Action Network (BAN), Silicon Valley Toxic Coalition (SVTC) and Computer TakeBack Campaign constitute a network of non-governmental organizations (NGOs) in the USA working together on E-waste issues, including international advocacy for the Basel Ban, domestic collection and recycling, and investigative research; the common objective is to promote national solutions for hazardous waste management (Widmer et al., 2005).

CONCLUSIONS

While E-waste grows within the developing world, technologies for its safe reuse or disposal have limited availability. Regulations, and their enforcement, have yet to become widespread. To limit hazardous E-waste mishandling, a variety of agreements and concerned organizations have come into being. Developed countries' systems for E-waste collection and disposal can provide models for the developing world. Conflict remains over hazardous waste export rules for producers.

REFERENCES

- UNEP (2007) E-waste volume II: E-waste management manual. Division of Technology, Industry and Economics, International Environmental Technology Centre, Osaka, Japan.
- USEPA (2007) Sustainable materials management: materials management and the 3Rs Initiative. <http://www.epa.gov/oswer/international/factsheets/ndpm-3rs-initiative-and-materials-management.htm>
- Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M., Boni, H. (2005) Global perspectives on E-waste. *Environ. Impact Assess. Rev.* 25:436-458.

CHARACTERIZATION AND FLOW ANALYSIS OF SUBSTANCES CONTAINED IN E-WASTE IN JAPAN FOR BETTER MANAGEMENT IN FUTURE

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INTRODUCTION

Waste electrical and electronic equipment (WEEE), or e-waste, has been an important target for appropriate management from the aspect of prevention of environmental pollution by hazardous substances. On the other hand, WEEE has recently received more attention as a secondary metal source. Japan has already introduced two recycling laws that cover eight types of equipment (TVs, refrigerators, freezers, air conditioners, washing machines, cloth dryers, PCs, and displays). In addition, recently some cities in Japan are collecting small electronics such as mobile phones and portable audio players on a trial basis because they contain precious metals and less common metals at a relatively high content. However, this is just a trial and much of WEEE that is not covered by the laws are collected and treated as municipal solid waste. According to the estimation by Oguchi et al. (2008), non-covered WEEE accounts for one-third of the whole amount of WEEE generated in Japan on a weight basis and this is still not a small amount. For the discussion toward better management of WEEE, this presentation introduces our investigations on characteristics and current flows of WEEE in terms of contained substances, particularly focusing on the non-covered WEEE.

CATEGORIZATION OF WEEE AS SECONDARY METAL RESOURCES

For the discussion toward more effective metal recovery from WEEE in future, the author and colleagues examined characteristics of WEEE as secondary metal resources on a specific equipment type level (Oguchi et al., 2011). Considering the analogy between natural resource development and metal recovery from WEEE, not only metal content but also total amount of metals contained in WEEE should be considered in secondary resource development. The author and colleagues categorized 21 types of WEEE into five groups according to their metal content and the total amount of metals in each equipment type and discussed their potential as secondary metal resources.

Fig.1 shows the examples of the categorization of WEEE according to metal content and the total amount of metals. CRT TVs, refrigerators, air conditioners, and washing machines (equipment types covered by the home appliances recycling law) had the highest content and the largest total amount of common metals; therefore, they could be the most important sources of common metals among the investigated equipment types. PCs, mobile phones, and video games were evaluated as the most important sources of precious metals in the same manner. Beside these equipment types, several types of small electronics were given second priority as sources of precious metals because they were categorized into the group with high content and moderate total amount of precious metals. However, in terms of total amount of metals, mid-size ICT equipment (e.g., printers) and audio/video equipment (e.g. VCRs) were at the same level as small electronics. Also, those mid-size equipment types were considered rather important as sources of the other metals including various less common metals in terms of total amount of metals as well as metal content. Recovering precious and less common metals from the mid-size equipment may not be economically feasible given current technologies; however, systems for collection, sorting, pre-processing, and metal recovery should be optimized considering the characteristics of each equipment type toward maximizing efficiency of metal recovery from WEEE.

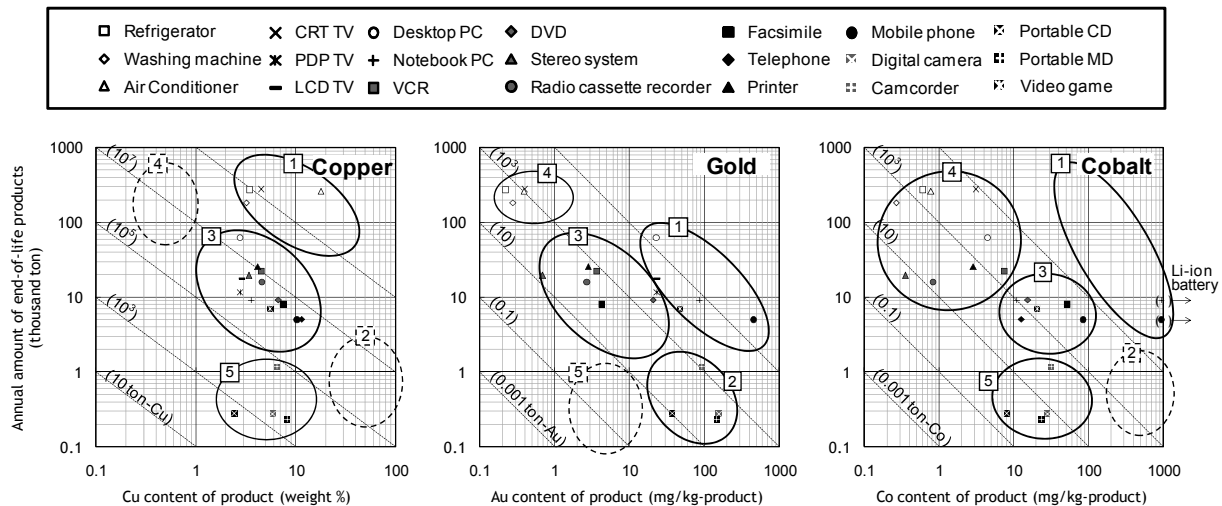


Fig. 1. Examples of categorization of WEEE from metal content and amount of end-of-life products. The dashed diagonal lines indicate the same amount of total metal. Product types within the ovals are in the same groups and the dashed ovals indicate empty groups.

FLows OF SUBSTANCES CONTAINED IN WEEE IN CURRENT MUNICIPAL WASTE TREATMENT SYSTEMS

In order to understand flows of substances contained in WEEE toward better resource recovery and management of hazardous substances, flows of 55 metals and organic compounds (e.g. brominated flame retardants) contained in WEEE during current municipal waste treatment system in Japan were investigated by conducting an experiment of WEEE treatment at a municipal waste treatment plant (Oguchi et al., 2011). The investigation revealed that a large part of various metals contained in WEEE that are not covered by the recycling laws are to be landfilled and never recovered in the current waste treatment systems. Through the shredding and separation process, approximately half of the Cu and three-fourths of the Al contained in WEEE were distributed to the large-grain fraction from sieving separation, which is subsequently treated by means of incineration and ash vitrification. Although Cu in this fraction is to be concentrated in molten-metal fraction through the thermal treatment processes and some of the Cu is to be recovered through copper smelting processes, more than half of the total Cu and most of the Al in the WEEE end up in landfills or dissipate in the current waste treatment systems. Among the other metals in WEEE, at least 70% of the mass was distributed to the small-grain fraction from the sieving separation and most of the metals in this fraction also end up in landfills.

CONCLUSIONS

Although the non-covered WEEE could be important metal source in terms of total amount of contained metals, a large part of the metals ends up in landfills through the current waste treatment in Japan. Domestic and international flows of the non-covered WEEE are still not fully understood and further study is needed toward better WEEE management in future.

REFERENCES

- Oguchi, M., Kameya, T., Yagi, S. and Urano, K. (2008) Product flow analysis of various consumer durables in Japan, *Resour Conserv Recycl.* 52: 463-480.
- Oguchi, M., Murakami, S., Sakanakura, H., Kida, A. and Kameya, T. (2011) A preliminary categorization of end-of-life electrical and electronic equipment as secondary metal resources. *Waste Manage.* in press.
- Oguchi, M., Sakanakura, H., Terazono, A. and Takigami, H. (2011) Fate of metals in waste electrical and electronic equipment: Distribution and substance flows in a municipal waste treatment process. *Waste Manage.* Submitted for publication.

RELEASE OF PERSISTENT TOXIC SUBSTANCES FROM UNCONTROLLED E-WASTE RECYCLING AND ACTIONS FOR OUR FUTURE

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INTRODUCTION

The recycling of e-waste including dismantling and burning will ultimately generate heavy metals and persistent organic pollutants to the surrounding environment and threaten human health (Wong et al, 2007). Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal was adopted on March 22, 1989 and entered into force on May 5, 1992. The USA being the world's largest e-waste producer, has not ratified either the Basel Convention or the Basel Ban Amendment. Approximately 20 years have passed. These communities are still debating the legal loophole which permits the export of whole products to other counties as long as it is not used for recycling (Wong et al, 2007). More scientific approaches are needed for solving the e-waste problem.

ACTION TO REPLACE PBDE

The Restriction of the Use of Certain Hazardous Substances (RoHS) in Electrical and Electronic Equipment (EEE) Regulations, 2006, prohibits and limits the use of certain materials including PBDE, PBB, Pb, Hg, hexavalent chromium, and Cd (OJEU, 2005). This is a good start but is it enough? It was concluded recently in 2006 that "Deca-BDE has long been characterized as an environmentally stable and inert product that was not capable of degradation in the environment, not toxic, and therefore of no concern." However, based on the debromination of deca-PBDE by photolytic reaction (Soderstrom et al, 2004) and anaerobic degradation reaction (Gerecke et al, 2005) to higher toxicity congeners, why shouldn't we also ban the use of deca-PBDE in electronic products (Illinois EPA, 2007)?

ACTION TO REPLACE PVC

Numerous studies have demonstrated that copper in copper wires acts as catalyst for the formation of PCDD/Fs during combustion of PVC. The burning of insulated wires generates 100 times more PCDD/Fs than domestic waste (Chan et al, 2007, Wang et al, 2009). Is there any technical reason for not replacing PVC insulation with other forms of plastic such as polyethylene for electronic applications?

RESPONSIBILITY AND OWNERSHIP OF E-WASTE

China WEEE Directive (Management Rule on Regulation and Treatment of Waste Electrical and Electronic Equipment) was implemented on January 1, 2011 provides stricter control over the import of e-waste in China, including Hong Kong, and demanding the principle of recycling e-waste is producer responsibility. If the current figures do not confirm China as the world largest electronic producer then it will very soon. The USA would still be the world's largest electronic user for a short while. According to UNEP, China is expected to overtake the United States as the principal producer of electronic waste by the year 2020.

CONCLUSION

Currently uncontrolled e-waste recycling generates persistent toxic substances and releases such compounds into the local environment. However, such persistent toxic substances

could end up into the ocean and would re-distribute into the environment and bioaccumulation, biomagnification might occur, and affect each of us in one way or another (Chen et al, 2009, Deng et al, 2007, Guan et al, 2009, Leung et al, 2008, Leung et al, 2010, Luo et al, 2007, Xing et al, 2010). Putting more effort into the design of future e-products from the perspective of minimal usage of any toxic metals and compounds, as well as selecting plastic components with limited release of toxic by-products from burning would be more fruitful than debating the definition of e-waste and responsibilities for handling the recycling.

REFERENCES

- Chan, JKY, Xing GH, Yu Y, Liang Y, Chen LX, Wu SC, Wong CKC, Leung CKM, Wong MH (2007) Body loadings and health risk assessment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at an intensive electronic waste recycling site in China. *Environ Sci Technol* 41:7668-74.
- Chen DH, Bi XH, Zhao JP, Chen LG, Tan JH, Mai BX, Sheng GY, Fu JM, Wong MH (2009) Pollution characterization and diurnal variation of PBDEs in the atmosphere of an e-waste dismantling region. *Environ Pollut* 157: 1051-7.
- Deng WJ, Zheng JS, Bi XH, Fu JM, Wong MH (2007) Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environ Int* 33: 1063-9.
- Gerecke AC, Hartmann PC, Heeb NV, Kohler HP, Giger W, Schmid P, Zennegg M, Kohler M (2005) Anaerobic degradation of decabromodiphenyl ether. *Environ Sci Technol* 39:1078-3.
- Guan YF, Sojiniu OSS, Li SM, Zeng EY (2009) Fate of polybrominated diphenyl ethers in the environment of the Pearl River estuary, south China. *Environ Pollut* 157: 2166-72.
- Illinois Environmental Protection Agency (2007). Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues. March 2007.
- Leung AOW, Duzgoren-Aydin NS, Cheung KC, Wong MH (2008) Heavy metals concentrations of surface dust from e-waste recycling and its human health implications in southeast China. *Environ Sci Technol* 42: 2674-80.
- Leung AOW, Chan JKY, Xing GH, Xu Y, Wu SC, Wong CKC, Leung CKM, Wong MH (2010) Body burdens of polybrominated diphenyl ethers in childbearing-aged women at an intensive electronic-waste recycling site in China. *Environ Sci Pollut R* 17: 1300-13.
- Luo Q, Cai ZW, Wong MH (2007) Polybrominated diphenyl ethers in fish and sediment from river polluted by electronic waste. *Sci Total Environ* 383: 115-27.
- Official Journal of the European Union (2005) Commission Decision of 13 October 2005 amending for the purposes of adapting to the technical progress the Annex to Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment.
- Soderstrom G, Sellstrom U, DeWit CA, Tysklind M (2004) Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environ Sci Technol* 38: 127-32.
- UNEP 2007 (United Nations Environment Programme, 2006 Annual Report)
- Wang F, Leung AOW, Wu SC, Yang MS, Wong MH (2009) Chemical and ecotoxicological analyses of sediments and elutriates of contaminated rivers due to e-waste recycling activities using a diverse battery of bioassays. *Environ Pollut* 157: 2082-90.
- Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AOW, Wong CSC, Luksemburg WJ, Wong AS (2007) Export of toxic chemicals – A review of the case of uncontrolled electronic-waste recycling. *Environ. Pollution* 149:131-40.
- Xing GH, Wu SC, Wong MH (2010) Dietary exposure to PCBs based on food consumption survey and food basket analysis at Taizhou, China – The world's major site for recycling transformers. *Chemosphere* 81: 1239-44.

HEALTH RISK ASSESSMENT OF ABANDONED FARM SOILS AFTER CHANGING LAND USE IN HONG KONG, ONE OF THE WORLD'S MEGA CITIES

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INTRODUCTION

In the 1980s, both abandoned and existing farmlands were dramatically changed to other land use purposes in Hong Kong due to rapid economic development and fragmentation (Li, 1998). Consequently, a substantial area of agricultural land has been changed to more profit-making uses such as storage sites (for containers, and construction waste), car dismantling workshops, and more recently, for storing, dismantling, recycling, and open burning of electronic waste (e-waste). The negative impacts of non-farming development on agriculture land can be more pervasive than the actual removal of land from farming via land use conversion (Berry et al., 1976). Direct and indirect impacts were the deprivation of land from agricultural production and pollution (Bryant and Johnstone, 1992). Consequently, non-conforming land uses may jeopardize both environmental and human health in terms of serving as a sink of pollutants in Hong Kong.

METHODS

Composite soil (275 samples) within 55 sampling sites were collected from the agricultural areas of Hong Kong and were classified into 12 different types based on land uses: agricultural soils (A), abandoned agricultural soils (Ab), organic farm soils (OF), container storage soils (CS), construction waste soils (CW), electronic-waste storage soils (EW (S)), electronic-waste dismantling workshop soils (EW (DW)), electronic-waste open burning site soils (EW (OBS)), open burning site soils (OBS), petrol station soils (PS), metal recycling workshop soils (MRW) and car dismantling workshop soils (CDW). Analyses of metal content (As, Cu, Cd, Cr, Pb, and Zn) and persistent organic pollutants (PAHs, PCDD/Fs, DDTs, HCHs, PBDEs and PCBs) in the soils were based on standard methods (U.S. EPA 1996a,b,c,d and US EPA, 1994). *In vitro* digestion model based on Ruby et al. (1996) was used to find out the bioaccessible pollutants concentrations. Subsequently, pollutants concentrations were used to establish Hazard Indices (for adults and children) and a cancer risk probability for humans (US EPA, 1997). In addition, Ames test (Ames et al. 1973), SOS chromotest (White et al., 1996) and EROD assay (Burke and Mayer, 1974) were used for testing the mutagenicity and genotoxicity of the soils respectively.

RESULTS AND DISCUSSION

The 95th centile values of Hazard Index (HI) of total elemental concentrations (As, Cu, Cd, Cr, Pb, and Zn) showed increased potential harm (HI = 1.16) for adults in EW (DW), while A, EW (DW) and CDW illustrated the most elevated non-cancer risks to children at 95th centile (6.65, 6.44 and 6.61 accordingly). Furthermore, PCDD/Fs WHO- TEQ levels in OBS and EW (OBS) indicated that HI far exceeded the unity with levels of 47.7 and 7.50 for adults, and 345 and 54.3 for children respectively. At 95th centile, soils of total elemental concentrations (As, Cd and Cr) from A, EW (DW) and CDW registered relatively high cancer risks (3.88×10^{-4} , 4.63×10^{-4} and 4.02×10^{-4} accordingly). Soil total PAHs in CDW indicated a high potential for cancer development (1420 in one million people). In addition, the levels of 17 PCDD/Fs congeners in OBS and CDW soils indicated high and moderate (6203 and 975 in one million people) cancer risks. Furthermore, soil total PCBs in EW (DW) and EW (OBS) show cancer risk development (40 and 2.1 in one million people). Ames test (Salmonella mutagenicity)

manifested that CDW soil had high mutagenic potency of 17.7 and 9.37 on both strains of TA 98 and TA 100, respectively, and relatively lower mutagenicity was observed for OBS and EW (DW) soils, with a mutagenic potency of 3.10 and 4.13, and 3.35 and 3.94, accordingly. SOS-ChromoTest indicated that soils of OBS, EW (DW), EW (OBS) and CDW had relatively high genotoxicity (SOS Inducing Potency of 1.01, 1.09, 1.56 and 1.68 respectively). EROD assay-derived 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) concentrations of the samples showed that OBS and EW (OBS) revealed the relatively high bioassay derived TCDD concentrations (935 and 517 pg/g). Based on the results of risk assessment and bioassay tests, soils from OBS, EW (DW), EW (OBS) and CDW showed the most prominent non-cancer risk, cancer risk, mutagenicity, genotoxicity and EROD assay-derived TCDD concentration. This suggested that changing agricultural lands to these types of land use might give rise alarmingly serious environmental and human health concerns.

CONCLUSIONS

As demonstrated by the non-cancer and cancer risk assessment, as well as the genotoxicity and mutagenicity tests, changing agricultural land use to open burning, car dismantling workshop and e-waste recycling are most hazardous to humans.

REFERENCES

- Ames, BN, Lee, FD, Durston, WE (1973) An improved bacterial test system for the detection and classification of mutagens and carcinogens. *Proc. Natl. Acad. Sci. USA*. 70:782-786.
- Berry, E, Leonardo, E, Bieri, K (1976) The Farmers' Response to Urbanization: A Study of the Middle Atlantic States. Philadelphia,
- Bryant, CR and Johnston, TRR (1992) Agriculture in the City's Countryside. Belhaven; London, England.
- Burke, MD and Mayer, RT (1974) Ethoxyresorufin:direct fluorimetric assay of a microsomal O-dealkylation which is preferentially inducible by 3-methylcholanthrene. *Drug Metab. Dispos.* 2: 583-588
- Li, YW (1998) Agricultural Land in Hong Kong: A Solution Space for Urban Development. M.S.c. Dissertation. Hong Kong: The University of Hong Kong
- Ruby, MV, Davis, A, Schoof, R, Eberle, S, Sellstone, CM (1996) Estimation of bioavailability using a physiologically based extraction test. *Environ. Sci. Technol.* 30: 422-430.
- US EPA (United States Environmental Protection Agency). (1997) Exposure Factors Handbook. Washington, DC: Environmental Protection Agency, Office of Research and Development. EPA/600/P-95/002F.
- US EPA (United States Environmental Protection Agency). (1996a) Method 3052: Microwave assisted acid digestion of siliceous and organically based matrices SW-846. Washington, DC.
- US EPA (United States Environmental Protection Agency). (1996b) Method 3540C: Soxhlet Extraction. Washington, DC.
- US EPA (United States Environmental Protection Agency). (1996c) Method 3620B: Florisil Cleanup. Washington, DC.
- US EPA (United States Environmental Protection Agency). (1996d) Method 8270C: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Washington, DC.
- US EPA (United States Environmental Protection Agency). (1994) Method 1613: Tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS
- White, PA, Rasmussen, JB, Blaise, C (1996) A semi-automated, microplate version of the SOS chromotest for the analysis of complex environmental extracts. *Mutat. Res.* 360: 51-74

HEAVY METALS AND POLYBROMINATED DIPHENYL ETHERS (PBDES) IN LEACHATES FROM AUSTRALIAN LANDFILLS: IMPLICATIONS TO ELECTRONIC WASTE MANAGEMENT

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INTRODUCTION

Electronic waste (e-waste) is one of the fast-growing problems in worldwide which is currently rising at over three times the rate of general municipal solid waste (ABS 2006). Approximately, 84 percent of e-waste in Australia are disposed in landfills (Environment Protection and Heritage Council 2009). Moreover, e-waste materials contain a variety of toxic substances which can contaminate the environment and threaten human health if not meticulous management. However, limited information exists in Australia on landfill leachates. For this reason we investigated the leaching of heavy metals and PBDEs from landfill process.

METHODS

Fresh and treated leachate samples were collected at leachate treatment ponds of 4 landfill sites in South Australia. Leachate samples were collected in 500 ml polyethylene container for heavy metals analysis and in 1000 ml amber bottle for PBDEs analysis (EPA 2007) which were transported to the laboratory and were stored at 4°C. Selected parameters: pH and electric conductivity (EC) were measured in the field. The concentrations of following heavy metals: Aluminium (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Lead (Pb), Antimony (Sb), Vanadium (V) and Zinc (Zn) were determined using ICP-MS and PBDEs were determined using GC-ECD.

RESULTS AND DISCUSSION

The pH of the leachate from 4 landfill sites showed similar pattern and values. In general, pH increases after the treatment process. EC of 4 sites vary considerable and range from 4.67 to 95.91 ms. Site D has the highest EC.

Appreciable levels of 14 heavy metals and PBDEs are detected in leachate from all 4 landfills although concentrations of heavy metals varied greatly. Sites A and D showed elevated concentrations of most heavy metals.

Twenty congeners of PBDEs (BDE-47, BDE-66, BDE-71, BDE-77, BDE-85, BDE-99, BDE-100, BDE-119, BDE-126, BDE-138, BDE-153, BDE-154, BDE-183, BDE-184, BDE-191, BDE-196, BDE-197, BDE-206, BDE-207 and BDE-209) were detected in leachates from all 4 landfills. Site D has the highest \sum PBDEs which is 22.93 $\mu\text{g/l}$ while 3 sites have $< 9 \mu\text{g/l}$. The concentrations of PBDEs in Australia are significantly higher than that reported for landfill leachates from Japan (Osako et al. 2004; Kim et al. 2006)

Table 1. The concentration of heavy metals and PBDEs

Leachate Constituent	pH -	EC mS	As µg/l	Co µg/l	Cr µg/l	Pb µg/l	∑PBDEs µg/l
Site A Fresh	8.21	15.17	109.04	36.78	253.73	7.91	4.10
Treated1	8.87	20.26	170.80	99.90	818.58	21.22	7.12
Treated2	9.31	29.30	234.11	162.80	1339.58	23.27	8.87
Site B Fresh	8.25	12.12	6.18	2.33	3.95	1.50	2.75
Treated1	9.51	14.28	77.44	0.93	5.87	2.43	3.67
Site C Fresh	7.78	17.46	120.75	27.13	223.95	1.13	4.27
Treated1	10.15	5.37	20.31	4.80	9.73	11.52	3.58
Treated2	10.38	4.67	9.81	1.25	3.09	1.06	4.29
Site D Treated1	9.26	95.91	198.84	59.35	2717.88	7.43	22.93

CONCLUSIONS

According to Gable and Shireman (2001) approximately 70 percent of heavy metals are released from e-waste. In this study the concentrations of heavy metals are fairly low whereas the concentrations of PBDEs are significantly higher than that reported elsewhere. Further, investigation is being conducted to estimate the toxicity of landfill leachates to environment.

REFERENCES

- ABS. (2006). "4613.0 - Australia's environment: Issues and trends, 2006." Environment snapshot: recycling up, but e-waste a looming issue Retrieved 7 December 2009, from <http://www.abs.gov.au/ausstats/abs@.nsf/mediareleasesbyTopic/FB2F33C170E4987DCA2572210077D0FA?OpenDocument>.
- Environment Protection and Heritage Council (2009). Decision regulatory impact statement: Televisions and computers: 257.
- EPA (2007). Method 1614 brominated diphenyl ethers in water soil, sediment and tissue by HRGC/HRMS. Washington, US, United States Environmental Protection Agency
- Gable, C. and B. Shireman (2001). "Computer and electronics product stewardship: Are we ready for the challenge?" Environmental Quality Management **11**(1): 35-45.
- Kim, Y.-J., M. Osako and S.-i. Sakai (2006). "Leaching characteristics of polybrominated diphenyl ethers (PBDEs) from flame-retardant plastics." Chemosphere **65**(3): 506-513.
- Osako, M., Y.-J. Kim and S.-i. Sakai (2004). "Leaching of brominated flame retardants in leachate from landfills in Japan." Chemosphere **57**(10): 1571-1579.

BODY LOADINGS AND HEALTH RISK ASSESSMENT OF DIOXINS AT AN INTENSIVE ELECTRONIC-WASTE PROCESSING SITE IN CHINA

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INTRODUCTION

Obsolete electronic waste (e-waste) has become a serious problem. The average lifespan of computers in developed countries has dropped from six years in 1997 to two years in 2005 (SVTC, 2005). According to the State Environmental Protection Administration of China, 70 % of the worldwide e-waste have been sent to China (Xinhua Online, 2007). The “recycling” of e-waste is done by primitive methods, which include burning piles of wire to recover metals, melting circuit boards over coal grills to release valuable chips, cooking computer casing to remove combustible plastics and isolate metals, and extracting metals in acid baths (Leung et al., 2006; Yu et al., 2006). These processes expose workers and local residents to toxic chemicals, and can lead to environmental contamination. In this study, we conducted health risk assessments of dioxins (PCDD/Fs) in Taizhou region (TZ), Zhejiang Province. This region is an intensive e-waste processing site in China and its e-waste recycling activities started in the late 70's. More than forty thousand people have been working in the e-waste recycling sector. The health risk assessment was also carried out at a reference site, namely Lin'an City (HZ), at Zhejiang Province, for comparison.

METHODS

Study population. Human milk, placenta, and hair samples were collected at the two study sites from 10 women who gave birth in 2005. Each set of specimens was collected from the same individual. Before the collection of specimens, the donors completed an informed consent. **Data collection.** Socio-demographic data and food consumption habits of the study population were obtained from face-to-face interviews and semi-quantitative food intake questionnaires, respectively. The response rate was 100%. **Sample collection.** Human milk (~ 100 ml) was collected from each donor when the infant was 4-5 days old. The sample was manually expressed and collected in hexane-rinsed reagent bottles with Teflon-lined caps. Placenta was collected on the day of delivery and individually placed into cleaned glass containers. Hair (~ 3 g) was collected on the 1st day after the delivery and was sampled from near the scalp and from the nape of the neck using stainless steel scissors. It was then put into a sealable polyethylene bag. All the specimens were frozen immediately after collection and stored at -20 °C until chemical analyses. **Laboratory analyses.** The analyses were conducted by The State Key Laboratory for Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Chinese Academy of Sciences, China. The details of the method could be referred to Chan et al. (2007).

RESULTS AND DISCUSSION

The total TEQ value of TZ human milk (21.02 ± 13.81 pg WHO-TEQ/g fat) was about two times higher than that of HZ human milk (9.35 ± 7.39 pg WHO-TEQ/g fat). TZ placenta

(31.15 ± 15.67 pg WHO-TEQ/g fat) and TZ hair (33.82 ± 17.74 pg WHO-TEQ/g dry wt) showed statistically higher concentrations than the samples from HZ (placenta: 11.91 ± 7.05 pg WHO-TEQ/g fat, hair: 5.59 ± 4.36 pg WHO-TEQ/g dry wt) ($p < 0.05$). Such heavy body burdens found in the mothers from the e-waste processing site (TZ mothers) could be explained by the background pollution level, dietary habit and personal characteristics of the sample donors. E-waste recycling operations, in particular, opening burning of e-wastes, could lead to high background levels. Extremely elevated levels of dioxins were found in soil sampled at the open-burning sites in Guiyu, another e-waste recycling site in China (Leung et al., 2007). Significant amounts of dioxin-related POPs, e.g. PAHs, were detected at the soil (Yu et al., 2006) and air samples (Deng et al., 2006) collected at areas near e-waste recycling workshops in Guiyu. On the other hand, according to the results of the food consumption survey conducted by this study, TZ mothers generally consumed more food of animal origin, whereby the consumption of pork and animal stomach were significantly higher ($p < 0.05$). Food of animal origin are considered to be the major dietary sources of dioxins since POPs are fat-seeking and accumulate in the fat of animals (Hooper et al., 1998). Results of statistical analysis showed that higher intakes of this food class led to greater body loadings in TZ mothers ($p < 0.05$) while the personal characteristics of sample donors were not a factor determining the dioxin body burdens.

CONCLUSIONS

Our results implicated that e-waste recycling operations could cause prominent PCDD/F levels in the environment and in humans. The elevated body burden may have health implications for the next generation. Work should be done on reducing the negative impacts caused by the e-waste recycling activities to the environments and humans. Moreover, further investigations on epidemiological study on the health impacts by e-waste recycling operations should be carried out.

REFERENCES

- Chan JKY, Xing GH, Xu Y, Liang Y, Chen LX, Wu SC, Wong CKC, Leung CKM, Wong MH (2007) Body loadings and health risk assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans at an intensive electronic-waste recycling site in China. *Environ Sci Technol* 41, 7668-7674.
- Deng WJ, Louie PKK, Liu WK, Bi XH, Fu JM, Wong MH (2006) Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM_{2.5} at an electronic waste recycling site in Southeast China. *Atmos Environ* 40: 6945-6955.
- Hooper K, Petreas MX, Chuvakova T, Kazbekova G, Druz N, Seminova G, Sharmanov T, Hayward D, She JW, Visita P, Winkler J, McKinney M, Wade TJ, Grassman J, Stephens RD (1998) Analysis of breast milk to assess exposure to chlorinated contaminants in Kazakhstan: high levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in agricultural villages of Southern Kazakhstan. *Environ Health Persp* 106: 797-806.
- Leung A, Cai ZW, Wong MH (2006) Environmental contamination from electronic waste recycling at Guiyu, Southeast China. *J Mater Cycles Waste Manage* 8: 21-33.
- Leung AOW, Luksemburg WJ, Wong AS, Wong MH (2007) Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in Southeast China. *Environ Sci Technol* 41: 2730-2737.
- STVC (2007) Just say no to e-waste: background document on hazards and waste from computers. <http://www.svtc.org/cleancc/pubs/sayno.htm>.
- Xinhua Online (2007) Seventy percent of worldwide electronic-waste goes to China. Dated January 1, 2007. http://news3.xinhuanet.com/tech/2007-01/09/content_5581834.htm (in Chinese).
- Yu XZ, Gao Y, Wu SC, Zhang HB, Cheung KC, Wong MH (2006) Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. *Chemosphere* 65: 1500-1509.

ASSESSMENT OF BIOACCESSIBILITY OF PCBs IN DIFFERENT FOOD USING AN IN VITRO DIGESTION MODEL

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INTRODUCTION

The consumption of contaminated food is an important route for human exposure to POPs. The extraction of pollutants from contaminated food using solvents may considerably overestimate the absorbed amount of contaminants contributing to the general health risk. Therefore, the bioavailability of various pollutants, in different food items, is an important factor for effective exposure estimation and health risk assessment.

In vitro digestion experiments are commonly used to study the bioaccessibility of heavy metals. In terms of POPs, there are only a few studies concerning their bioaccessibility in soils. There is a lack of information concerning the bioaccessibility of organic pollutants in food.

Polychlorinated biphenyls (PCBs) were used in this research as model chemicals because PCBs are universal toxic chemicals in food and have great influence on human health. The objectives of this research were to: (1) develop an *in vitro* digestion method for analyzing bioaccessibility for PCBs in food; and (2) investigate the differences in digestion efficiencies for PCBs in different food items and identify their contributing factors.

METHODS

Sample collection and pretreatment

Oriental weather fish (*Misgurnus anguillicaudatus*), bighead carp (*Aristichthys nobilis*), spinach (*Spinacia oleracea*) and cabbage (*Brassica oleracea*), collected from Taizhou (Zhejiang Province, China), which is a main electronic waste recycling site in China, were chosen for this study because they are commonly consumed by the local people and also because of their relatively high concentrations of PCBs according to our preliminary food surveys. All the samples of the same food items were washed, freeze-dried, pooled and homogenized prior to extraction.

Laboratory analysis

Determination of digestible fraction followed the method described by Goñi et al., (2006) and Cabañero et al. (2004) with slight modification. Briefly, vegetable and fish samples were sequentially incubated with a series of enzymes, including pepsin, pancreatin, lipase, bile extract, and α -amylase. Samples were then centrifuged, and then filtrated with a glass fiber membrane (0.45 mm). The supernatants were extracted using liquid-liquid shaking method, and the solid samples with filters were extracted in a Soxhlet apparatus.

All the extracts were cleaned-up through multilayer silica gel column and florisil column, and then thirty-six PCB congeners were quantitatively analyzed by GC-MS (Hewlett Packard 6890 GC coupled with a 5973 MS selective detector).

Calculation of bioaccessibility

Bioaccessibility of chemicals in this study can be defined as the fraction of the contaminants mobilized into the digestive juices from food which would be available for absorption through

the small intestine. The bioaccessibility of PCBs were calculated as the ratio of the amount of PCBs in liquid phase to that in the sum of liquid and solid.

RESULTS AND DISCUSSION

The average bioaccessibilities of PCBs in bighead carp, oriental weatherfish, spinach and Chinese white cabbage were 2%, 3%, 25% and 27%, respectively. The variations of accessibility among different congeners in fish were larger than in vegetables. WHO-PCB-TEQ₁₉₉₈ values for the digestible portion in bighead carp, oriental weather fish, spinach and cabbage were 1.01, 0.64, 0.82 and 0.31 pg/g dry wt, respectively, which accounted 2, 3, 11, and 30%, respectively, for the original total TEQs. Based on our survey in Taizhou, the ratio of the contribution to human dietary exposure from the consumption of freshwater fish and leafy vegetables was 85:15. However, if bioaccessible intake was taken into account, these values would change to 59:41. The human health risk exerted by PCBs in the food matrix was substantially lowered during the process of digestion, especially in fish.

The influences of physico-chemical properties of PCBs on bioaccessibility were analyzed, based on the relationships between different parameters including K_{OA} , K_{OW} , molecular weight (MW), water solubility and bioaccessibility of PCB congeners. Significant negative correlations ($p < 0.05$) were observed between K_{OA} , MW and bioaccessibility for three food items (bighead carp, spinach and Chinese white cabbage). Perhaps for low-lipid food, physico-chemical parameters such as K_{OA} , K_{OW} , MW and water solubility could be employed to predict the approximate bioaccessibility of PCBs in the future. In terms of fish, especially for oriental weatherfish which had relatively high lipid content, most PCBs were sequestered in food thereby making them difficult to release from the food matrix.

CONCLUSIONS

Although only two kinds of food samples were analyzed for each food item (fish and vegetables), the results showed differences of bioaccessibility of PCBs between vegetables and freshwater fish. This study draw attention to the importance of incorporating bioaccessibility as a part of the risk assessment process and provide a practical estimation of human exposure and health effect assessment for PCBs.

REFERENCES

- Cabañero, A.I., Madrid, Y., Cámara, C. (2004) Selenium and mercury bioaccessibility in fish samples: an in vitro digestion method. *Anal. Chim. Acta* 526:51 - 61.
- Goñi, I., Serrano, J., Saura-Calixto, F. (2006) Bioaccessibility of β -carotene, lutein, and lycopene from fruits and vegetables. *J. Agric. Food Chem.* 54: 5382 - 5387.
- Intawongse, M., Dean, J.R. (2006) *In vitro* testing for assessing oral bioaccessibility of trace metals in soil and food samples. *Trends Anal. Chem.* 25: 876-886.
- Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., Van de Wiele, T., Wragg, J., Rempelberg, C.J.M., Sips, A.J.A.M., Van Wijnen, J.H. (2002) Comparison of five *in vitro* digestion models to study the bioaccessibility of soil contaminants. *Environ. Sci. Technol.* 15: 3326 - 3334.
- Xing, G.H., Wu, S.C., Wong, M.H. (2010). Dietary exposure to PCBs based on food consumption survey and food basket analysis at Taizhou, China - The World's major site for recycling transformers *Chemosphere* 81:1239 - 1244.

CONCENTRATION OF ARSENIC IN HOME GROWN VEGETABLES

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INTRODUCTIXON

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). Intake through consumption of home grown produce is of concern not only in developing countries but this approach may also be valuable when dealing with brown-fields site redevelopment. 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 of the surveyed families from home grown 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. All samples except cooked vegetables were washed three times with tap water followed by de-ionized water. Vegetables were dried in the open air for 24 h, followed by oven drying at 65°C to complete dryness. Then the samples were homogenized by grinding with a stainless steel grinder. Concentrated nitric acid was used for the digestion of samples. Total As was estimated using the digestion procedure of Rahman et al. (2009b). An Agilent 7500c (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of As in vegetables. The vegetables consumption rate for adult males and females (n = 71, age range 12-80 years) was an average 205g (median: 200g).

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 mean and median concentrations of As in all vegetables were 113 µg/kg and 90 µg/kg, respectively. The range of As in vegetables was 11-464 µg/kg. Alam et al. (2003) reported that the range of As in home garden vegetables from Samta village of Bangladesh was 19-489 µg/kg. The range of As in vegetables from Chandpur and Jamalpur districts was 70-3990 µg/kg (Das et al. 2004) and from Sathkhira, Rajshahi and Comilla districts was <40-1930 µg/kg (Williams et al. 2006). 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). On the other hand, the mean and median As concentrations of non-leafy vegetables was 45 µg/kg

and 30 µg/kg (range: 11-145 µg/kg). The range of As in non-leafy vegetables (fruit, root and tuber) from Sathkhira, Rajshahi and Comilla districts was <40-1930 µg/kg (Williams et al. 2006). Arsenic level was much lower for both leafy and non-leafy vegetables in our study compared to the study of Williams et al. (2006). The uptake of heavy metals in vegetables from soil varies from area to area depending on the concentrations of heavy metals in soils and irrigation water.

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. This was attributed to the use of As-safe pond water for cooking by all families.

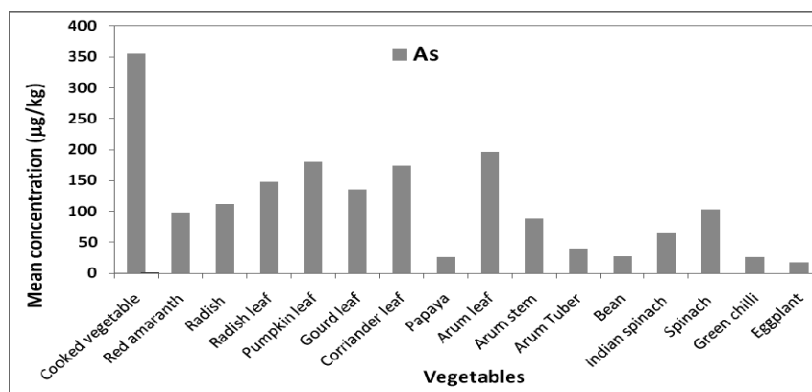


Fig. 1. Concentrations of As in home grown vegetables

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. Although we collected various types of commonly consumed vegetables from the study area, this does not representative of all vegetables consumed by the populations in other areas of Bangladesh. The food survey should not restrict on As only, other heavy metals such as Cd, Pb etc. also need to be monitored regularly.

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.

INDUSTRY-WIDE APPROACHES TO RISK ASSESSMENT: A CASE STUDY OF COPPER IN AUSTRALIAN VINEYARDS

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INTRODUCTION

Companies are under increasing pressure to demonstrate their environmental responsibility by meeting the expectations of regulators, markets, consumers, and the general public. However, risk assessment studies can be costly, particularly for small enterprises. Where there is a common issue it may be more beneficial to adopt a collaborative industry-wide approach. This paper presents a project which adopted an industry wide approach to assess the environmental risks associated with copper-based fungicide residues in Australian vineyard soils.

Copper-based fungicides have been regularly applied in vineyards for many decades to protect against fungal diseases. However, their use results in an accumulation of Cu in surface soils. For instance, Cu concentrations ranging from 130 to 1280 mg/kg have been detected in the surface soils of European vineyards (cf. background of <20 mg/kg Cu) (Wightwick et al, 2010). The surface-accumulated Cu is not expected to cause phytotoxicity in mature grapevines. However, it may cause negative effects to soil biota (e.g. earthworms, micro-organisms) and impact on the long-term biological health and fertility of the soil (Wightwick et al, 2010). Australian viticultural industries require quantitative information on the environmental risks posed by Cu-based fungicides to assist in formulating evidence-based policy decisions for the future management of Cu in vineyards.

RISK ANALYSIS STUDIES

Adopting an industry wide approach to assessing the risks of Cu presented a particular challenge in the Australian context as there are approximately 60 viticultural production regions covering a wide variety of soil types (i.e. influencing Cu bioavailability) and climatic conditions (i.e. influencing disease pressure). In the first phase of field investigations a composite surface soil sample (0 – 10 cm depth) was collected from each of 98 vineyards (with histories of Cu-based fungicide use) encompassing 10 viticultural regions of Australia and a range of soil types (i.e. pH 5 – 9.8). Ninety-six percent of the vineyards had elevated total Cu concentrations compared with nearby 'clean' reference soils. Total Cu concentrations in the vineyard soils were as high as 223 mg/kg; however the majority were only moderately contaminated (~50% between 25 – 75 mg/kg total Cu). The bioavailability (CaCl₂ extractable) of the accumulated Cu was relatively low, with < 0.5 % of total Cu in the majority of vineyard soils; and closely related to the total Cu concentration, pH and clay content of the soil. The soil Cu concentrations were compared to reported ecotoxicological data. This indicated that Cu-based fungicide residues in Australian vineyard soils may be causing harm to earthworms and microbial processes. For instance, 44% of vineyards exceeded an estimated sub-lethal hazardous concentration (HC₅) value of 55 mg/kg total Cu. However, it was difficult to make definitive conclusions on the risks as reported ecotoxicological values vary widely across soil types (i.e. EC₅₀ nitrification, < 100 to >1000 mg/kg total Cu; Oorts et al, 2006).

The second phase of the study involved the use of direct toxicity assessments to more definitively determine the risks to soil microbial functions in Australian vineyard soils. The accumulation of Cu-based fungicide residues has occurred over many years thus providing plentiful opportunity for Cu-aging in the soil (reducing bioavailability) and for soil organisms to adapt to the increased Cu. Therefore, toxicity assessments with field contaminated soils were preferred over the use of 'artificially' contaminated soils. Composite soil samples were collected from vineyards and nearby 'clean' reference locations at 10 sites in each of three viticultural regions in Australia; representing acidic, neutral and alkaline soils. The soil samples were incubated in the laboratory for 54 days under common conditions and the microbial function measured using enzyme activities related to N, P, C and S cycling in soils. At specific sites the vineyard soils generally had greater concentrations of Cu and lower enzyme activities than in the 'clean' soils; pointing towards an adverse effect of Cu-based fungicides. However, using the power of the industry wide approach, trend analysis across all sites showed little evidence of adverse effects of Cu-based fungicide residues. Rather, microbial function was being driven predominately by physical-chemical soil properties (i.e. organic C, pH). There was some indication that the accumulated Cu may be harming microbial mediated P cycling processes in Australian vineyard soils.

The risk analysis suggested that active risk management action is not yet required to mitigate the risks posed by Cu-based fungicide residues in Australian vineyard soils. However, globally there are societal and regulatory pressures to move towards restrictions on Cu-based fungicide use. As such, there is likely to be an increase in the use of alternative synthetic organic fungicide compounds. However, assurances are needed to ensure they are in fact safer for the environment. Laboratory experiments suggested that the alternative fungicides, such as captan and trifloxystrobin, are likely to pose a lower long-term risk to soil microbial function compared with Cu-based fungicides. However, other studies suggest that fungicide residues may pose a risk to aquatic ecosystems due to off-site migration (i.e. via leaching, runoff, spray drift) (Wightwick et al, 2010). For instance, a study at 18 sites within a horticultural production catchment in Victoria (Australia) detected fungicide residues in 63% of water samples and 44% of sediment samples (unpublished). A total of 17 different fungicide compounds were detected, with 31% of water samples containing residues of two or more fungicide compounds. However, at present there is relatively little ecotoxicological data available for fungicides for which to indicate the risks.

CONCLUSIONS

The viticultural and wine industry in Australia utilises national environmental stewardship programs to demonstrate its environmental credentials in order to maintain and enhance access to domestic and international markets. Negative perceptions about Cu-based fungicide use have the potential to harm the environmental credentials of the industry. Scientific evidence has been generated on the environmental risks posed by Cu-based fungicides which the industry can now use for environmental reporting, benchmarking against viticultural/wine industries in other countries, and formulating evidence-based policy decisions on the future management of Cu-based fungicides. Adopting the industry-wide approach enabled a more comprehensive and powerful assessment of the environmental risks. Smaller site specific studies may have overestimated the environmental risks potentially leading to unnecessary risk management action.

REFERENCES

- Oorts, K., Ghesquiere, U., Swinnen, K., and Smolders, E. (2006). Soil properties affecting the toxicity of CuCl_2 and NiCl_2 for soil microbial processes in freshly spiked soils. *Environmental Toxicology and Chemistry*. 25:836-844.
- Wightwick, A., Walters, R., Allinson, G., Reichman, S.M., and Menzies, N.W. (2010). Environmental risks of fungicides used in horticultural production systems. In: Carisse, O. (Ed.). *Fungicides*. InTech, Reijka, Croatia, pp. 273 - 304.

REMEDIATION OF A PLUME OF ACIDIC ZINC CONTAMINATED GROUNDWATER IN YAGOONA, NSW

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INTRODUCTION

Historical practices at a galvanising plant in western Sydney have resulted in contamination of the underlying shallow aquifer, with the principal contaminant being zinc, and lesser amounts of other metals in highly acidic groundwater (i.e. pH < 3). The site is underlain by fill materials and clay rich soils, which in turn are underlain by weathered shale bedrock hosting a shallow semi-confined low-yielding aquifer. The acidic plume of metal impacted groundwater is confined to the operational part of the site, where galvanising operations are carried out. The impact decreases down-gradient of the operational area with no apparent impact off site. Various improvements have been undertaken at the site, including relining of the acid galvanising baths to mitigate the environmental impacts.

Numerous environmental assessments have been conducted at the site to characterise the contamination and for the purpose of understanding whether conditions are suitable for monitored natural attenuation. The site is currently under regulation as a contaminated site by the NSW Department of Environment, Climate Change and Water (DECCW) under the Protection of the Environment Operations Act 1997.

METHODS

A network of groundwater monitoring wells has been installed both on and off site to achieve delineation of the contamination. Groundwater was monitored on a quarterly basis for geochemical parameters (i.e. pH, electrical conductivity, reduction-oxidation potential and dissolved oxygen), contaminants of potential concern (i.e. zinc, ammonia, lead, cadmium, copper, nickel and arsenic) and other key chemical parameters including major cations and anions. The groundwater chemistry was assessed using hydrochemical plots such as piper and stiff diagrams and the relationship between dissolved metal concentrations and pH evaluated. The relationship between zinc and pH is shown in Figure 1 and follows the predicted trend of zinc mobilising below pH 5 (Drever, 1997).

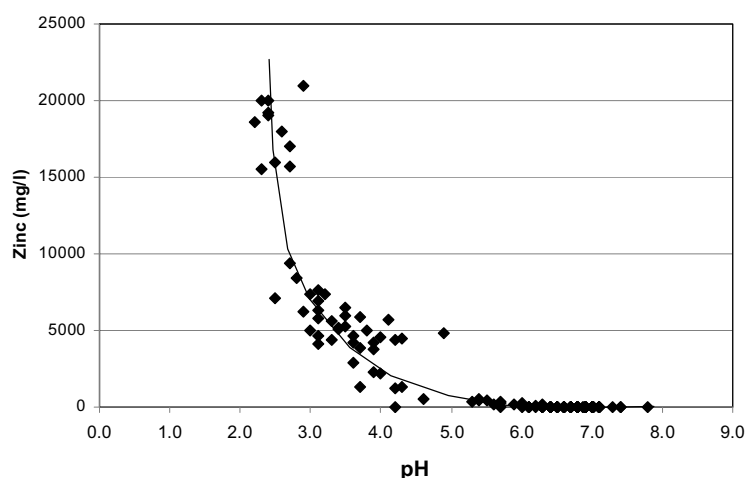


Fig. 1. Dissolved zinc concentrations from site groundwater as a function of pH, showing the predicted mobilisation of metals under strongly acidic conditions.

REMEDIATION STRATEGY

An initial strategy was adopted to use a monitored natural attenuation (MNA) approach to remediate the groundwater at the site. While metals do not degrade in the way that organic contaminants do, it could be demonstrated that the impacted area was stable and the aquifer permeability and yield were low. Therefore, a MNA approach was considered appropriate to demonstrate that remediation was sufficient.

However, the DECCW considered the site a significant risk of harm and requested that an active remediation approach be adopted. After assessing various in situ and ex situ options, and taking into consideration DECCW endorsed guidance on remediation, two remedial options were considered feasible. The first was extraction and treatment of impacted groundwater and the second was injection of an alkaline agent to treat the groundwater in situ. Based on the low permeability and yield, it was considered impractical to consider injection into the aquifer. Therefore an approach of passive extraction and treatment over a medium to long term period, with regular monitoring of success was selected as the preferred remedial strategy, which was subsequently endorsed by DECCW.

A system was designed and constructed by using air compressor-driven submersible pumps, installed into monitoring wells in the source zone, reticulated on a manifold and connected to a receiving treatment tank for dosing and subsequent disposal. To save costs and provide a more sustainable approach, existing monitoring wells were used for extraction with low volume small-scale pumps and tubing chosen that were applicable to expected low yields of the aquifer.

The system is currently under construction and is anticipated to be commissioned in April 2011 and will be in operation for at least one year prior to reassessment and possible decommissioning.

CONCLUSIONS

An effective pump and treat system was designed for the site, which will extract contaminated groundwater over a medium to long term basis, causing a cone of depression and allowing natural un-impacted groundwater to flow back into the aquifer. However, given that site operations are no longer contributing to the groundwater contamination source and the plume is stable and poses no health or ecological risk, it is debatable whether active remediation provides the most sustainable solution for this site.

REFERENCES

- Drever, J.I. (1997) *The Geochemistry of Natural Waters: Surface and Groundwater Environments*. Third Edition. Prentice Hall Inc. Upper Saddle River, NJ. 436p.
- GHD (2010) *Report for 117 – 153 Rookwood Road, Yagoona, NSW: Monitored Natural Attenuation Assessment Program, November 2010*. Report reference: 21/13887/165379.
- GHD (2011) *Yagoona Zinc Galvanising Plant: Groundwater Remedial Action Plan*. Report reference: 21/20200/166676.

A MAGIC WEED TO WEED OUT CHROMIUM CONTAMINATION

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INTRODUCTION

The continuous influx of toxic heavy metals including chromium (Cr) into the environment leads to the contamination of both soil and water. A complex variety of biotic and abiotic pathways determine the fate and speciation of Cr in the soil. While hexavalent Cr [Cr(VI)] is highly toxic, mobile and influences human health, the trivalent Cr [Cr(III)] is non-toxic and less mobile. Chromium toxicity in soils can be mitigated by reduction of Cr(VI) to Cr(III) which is controlled by the presence of free Cr(VI) species in soil solution, supply of protons and electrons. Recent trends of removal of Cr(VI) by means of addition of biomass as bio-sorbents and bio-reductants for Cr(VI) has been increased due to cost effective remediation technique (Mohan and Pittman, 2006). The mobility, toxicity and bioavailability of Cr depends on its oxidation state, so the best strategy to remediate Cr(VI) contamination is to reduce soluble, mobile and toxic Cr(VI) to insoluble and relatively less toxic Cr(III) (James, 2001).

In this study, the effect of black carbon obtained from a local weed species (*Solanum elaeagnifolium*) on the reduction and mobility of Cr(VI) in acidic and alkaline soils was investigated.

METHODS

Two different soils were collected from uncontaminated sites in Adelaide Hills (ADH) and Kulpara Bay (KPB) in South Australia. Black carbon (BC) was prepared from south Australian common weed plant *Solanum elaeagnifolium*. The plant material was dried, treated with HCl and HCl-HF for protonation and to remove silica and other inorganic materials, respectively and washed several times with MilliQ water until there was no change in pH of material. Black carbon was dried in oven at 60°C and stored in a glass container.

The soil and black carbon samples were analysed for pH, total organic carbon. For the Cr(VI) reduction experiment, the soil samples were first treated with 0 and 500 mg/kg of Cr(VI) and then amended with protonated and unprotonated BC (5%). The Cr(VI) treated and black carbon amended soil samples were incubated at field capacity. The concentration of Cr(VI) in soils was measured periodically using 1M KH₂PO₄ as an extracting solution and the rate of Cr(VI) was calculated. For the leaching experiment, both acidic and alkaline soils were incubated with 500 mg Cr(VI)/kg soil and subsequently mixed with protonated black carbon (5%) and incubated for three days at field capacity. The treated soils were packed in columns and leached with 0.001M CaCl₂. The leachate Cr(VI) concentration was measured colorimetrically using Diphenyl Carbazide as color developing reagent.

RESULTS

The pH varied from acidic (4.60) in ADH soil to alkaline (8.17) in KPB soil. Organic matter was in the range of 1.06 to 6.7% and pH of protonated and unprotonated BC was 3.5 and 8.3, respectively.

Reduction of Cr(VI) in soils

The results indicated that protonated black carbon is highly effective in reducing Cr(VI) in both acidic and alkaline soils examined. The concentration of Cr(VI) decreased 185.8 and 141.4 mg/kg in acidic and alkaline soils (500 mg/kg), respectively after 14 days incubation.

However, black carbon (5%) addition decreased 487.47 and 491.78 mg/kg in 4 and 10 days, respectively (Fig. 1a).

The high efficiency of BC may be attributed to the presence of several oxygen containing acidic (carbonyl, lactonic, carboxylic, hydroxyl and phenol) and basic (chromene, ketone and pyrone) functional groups. Black carbon is composed of several fused rings, stacked as polycyclic aromatic sheets. The edges of these sheets are reactive with various functional groups, which donate electrons for Cr(VI) reduction. The resultant Cr(III) participates in either adsorption or surface complexation. (Hsu et al., 2009).

Leaching of Cr(VI) in soils

Chromium(VI) leached more from alkaline soil than acidic soil. In acidic and alkaline soils, 14.55 and 33.23% of total added Cr(VI) was leached, respectively in 3 days incubation time. Addition of BC (5%) decreased the leachable Cr(VI) to 4.08 and 10.65 % of total added Cr(VI) in acidic and alkaline soils, respectively (Fig. 1b). The effect of addition of BC on mitigating Cr(VI) leaching was more pronounced in alkaline soils. Black carbon in the amended soils reduced Cr(VI) to Cr(III), the reduced Cr species have less mobility, thereby retarding Cr transport (Bolan et al., 2003).

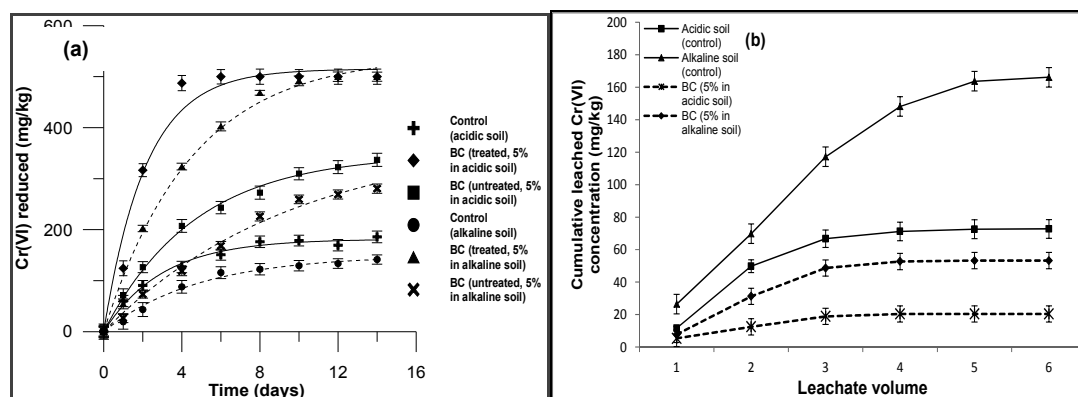


Fig. 1(a). Effect of black carbon on reduction of Cr(VI); (b). Leaching of Cr(VI) in acidic and alkaline soils before and after treatment with black carbon.

CONCLUSIONS

Black carbon prepared from the local weed was found to be effective in decreasing Cr(VI) mobility through reduction mechanism. Addition of black carbon enhanced the reduction of Cr(VI) and the effect was more pronounced in alkaline soils. The leaching of Cr(VI) is higher in alkaline soils and again the addition of black carbon decreased Cr(VI) leaching and transport in soils.

REFERENCES

- Bolan, N.S., Adriano, D.C., Natesan, R, Koo, B.J. (2003) Effects of organic amendments on the reduction and phytoavailability of chromate in mineral soil. *J. Environ. Qual.* 32: 120-128.
- Hsu, N.H., Wang, S.L., Lin, Y.C., Sheng, G.D., Lee, J.F. (2009) Reduction of Cr (VI) by crop-residue-derived black carbon. *Environ.Sci.Technol.* 43: 8801-8806.
- James, B.R. (2001) Remediation-by-reduction strategies for chromate-contaminated soils. *Environ. Geochem. Health.* 23:175-179.
- Mohan, D., Pittman Jr, C.U. (2006) Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *J. Hazard. Mater.* 137: 762-811.
- Walkley, A. & Black, I.A. (1934) An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science* 37: 29-38.

HUNTER RIVER REMEDIATION PROJECT – DELIVERING ENVIRONMENTAL EXCELLENCE AT AUSTRALIA’S LARGEST REMEDIATION PROJECT

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INTRODUCTION

BHP Billiton’s Hunter River Remediation Project (HRRP) involves the dredging, treatment, transport and emplacement of more than 800,000m³ of contaminated sediment removed from the South Arm of the Hunter River. The HRRP is the largest remediation project of its kind to be undertaken in Australia.

The sediment was contaminated by activities of the former BHP-owned Newcastle Steelworks that operated from 1915 until its closure in 1999. During the 1930s, the Newcastle Steelworks was the largest Steelworks in the Commonwealth and for much of its life provided significant economic stimulus for the region and wider state and national economies.

For much of the Steelworks’ existence, the stringent environmental standards and legislation prevalent today did not exist and so, over time, some by-products from steel-making made their way into the neighbouring Hunter River.

The remediation is being done to satisfy the environmental requirements of BHP Billiton’s own standards, the *Contaminated Land Management Act 1997* (NSW) and requirements of the river bed landowner, NSW Maritime.

The main contaminants found in the river sediments are derived from coal tar residues, in waste streams, associated with the coke oven and other heavy plant operations at the former Steelworks. The main sediment contaminants are Polycyclic Aromatic Hydrocarbons (PAHs), primarily naphthalene, Benzo(a)pyrene (BaP), Total Petroleum Hydrocarbons (TPH) C10-C36 and to a lesser extent some metals. Volatile Organic Compounds (VOCs), including BTEX comprising Benzene, Toluene, Ethylbenzene and Xylene, are also found within the sediments.

The HRRP has been implemented in accordance with sustainable development principles and with no adverse impacts on river health recorded from a comprehensive environmental monitoring program that has involved approximately 250,000 environmental measurements. There has also been widespread community support for the HRRP as evidenced from survey and other feedback mechanisms, including the HRRP Community Consultative Committee (CCC).

The HRRP’s environmental system and results are world-class and have been regarded by many as setting a new benchmark. This has been acknowledged by industry peers, regulatory authorities and the United Nations Association of Australia (UNAA) in their awarding of the HRRP the major industry winner for Environmental Best Practice Program at the World Environment Day Awards 2011.

The HRRP commenced dredging around mid 1999 and is currently 95% complete. The project remains on track for completion in late 2011. The HRRP total cost is in the order of \$600 million.

METHODS

Specialised dredging equipment and operational controls, including GPS, environmental clamshell buckets, sheet pile walls and silt curtains, are used to accurately recover the river sediment in a manner protective of river quality.

Dredged sediment is then transferred a short distance by barge and unloaded and treated at the former Steelworks site at Mayfield. The treatment is cement stabilisation (immobilisation) which is a proven and NSW EPA-approved treatment method for this type of contaminated sediment.

After treatment, the sediment is transported by truck to a new landfill facility on former industrial lands at nearby Kooragang Island. From here, treated sediment is emplaced within discrete cells that feature innovative controls to protect the local environment contributing to its unique design.

Upon capping completion, the landfill facility will be monitored by BHP Billiton for a period of up to 15 years to ensure long-term environmental, engineering and land-use objectives are met.

RESULTS

The HRRP, which has significant and complex risk and regulation, was recipient of this year's UNAA Environmental Best Practice Program Award for its remarkable environmental record.

In addition to the permanent removal of more than 800,000m³ of contaminated sediment from the river system, notable environmental achievements include:

- Nil pollution events
- Nil impacts on river health
- Nil significant environmental incidents
- >250,000 monitoring measurements, no material impacts
- 100% validation success from 500 core samples confirming a cleaner river
- >99% compliance against 3,500 approval actions from 260+ statutory approvals
- Conservation of >85% of breeding habitat for the endangered Green and Golden Bell Frog and 100% of local mangroves from unique emplacement design
- Design and implementation of a benchmark compensatory habitat program for the Green and Golden Bell Frog

CONCLUSIONS

The cleanup standards which have been applied to the HRRP represent some of the most environmentally-protective of anywhere in the world and, in many cases, these standards exceed the statutory requirement as part of BHP Billiton's overriding commitment to Zero Harm.

The HRRP represents a new model in effective river remediation that delivers on its primary environmental objectives by adopting benchmark systems that are founded on core values and sustainability principles, contributing to its standing as a case study of leading industry practice.

SPREADING OF SLIGHTLY POLLUTED SEDIMENT ON AGRICULTURAL LAND

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INTRODUCTION

In the Dutch water management system, ditches have an important function in discharge of surplus of water during wet periods and supply of water during dry periods in the growing season in summer. Without maintenance of the system they become silted up by caving in of the bank, sedimentation of particles present in water coming from other areas, and from residuals of vegetation. Vegetation in most ditches is removed yearly, and the sediment in the ditches is dredged every 6-10 years. In the past, spreading of dredged sediments was not a problem, for dredged sediments have a fertilising function and are used to level fields. Sediments are spread on the banks of the adjacent agricultural fields in a layer of several to about 20-30 cm (depending on dredging method and density of the sediment). When the sediment is dewatered and partly ripened the farmer spreads levels the field (grassland), plough the soils and grows crops on it (arable land).



Spreading of sediments on agricultural land

Since we know that sediments contain contaminants such as PAHs and heavy metals (sediments act as a sink for contaminants) it is not allowed anymore to spread all available dredged sediments. Spreading is limited to clean or slightly contaminated sediments. It is questionable if spreading of slightly contaminated sediment is sustainable as it may lead to accumulation of contaminants in agricultural land and may have impact on the quality of the agricultural products. This research has been started to determine the effect of spreading of sediment on soil quality.

METHOD

Locations were selected in regions with clay soils where slightly contaminated sediments have been spread during last decades (based on data present at Water Boards).



Storage of sediment in a depot

We selected the locations where according to the Water Boards the sediments had the highest levels of contamination (within the Dutch regulation for spreading). On every selected location the sediment, the part of the agricultural field where sediment has been spread and the part where no sediment has been spread (Reference) were sampled. Spreading of sediment is the only difference in the samples taken on the agricultural field and all other activities were responsible for the background in both areas.

In regions with peat soils the practise of

spreading sediment has changed and sediments were collected on relative low-lying fields, in order to elevate the level (depots). After ripening of the sediment the elevated fields are taken into agricultural practise again. The elevated fields and reference neighbouring fields have also been sampled.

Samples were analysed on heavy metals and organic contaminants. Special attention has paid to the bioavailability of the contaminants. Bioassays were used in a selection of the samples.

Results of the practical study were supported by a model study in which accumulation is calculated as the results of all inputs (e.g. sediment, air, manure) and outputs (e.g. leaching, uptake by crops, biodegradation).

RESULTS

Clay areas

- The sediments spread are relatively clean, maximum allowable concentration are mostly not present and very often concentration are just above the criteria for clean sediments.
- The effect of spreading on the accumulation of heavy metals is not recognizable on most locations. The background concentration (Reference) is the most important factor for the concentration found. Increase of the actual bioavailable amount is observed, which could be explained by the pH.
- For PAHs, accumulation could be observed. The bioavailability of the PAH is low, which means that biodegradation is a slow process and the degradation is not fast to eliminate the addition of new PAHs in after spreading of new sediment. On the other hand a low bioavailability also means a low risk.
- Modeling results show that accumulation is stronger with a large difference in quality between sediment and soil on the agricultural land. The model is suitable to do simulations with different sediment qualities.

Peat areas

- In the depots a thicker layer of sediment is used and no dilution occurs due to mixing with the original soil. The sediment quality is also the quality of the soil obtained after ripening (heavy metals)
- Content of PAHs slowly decreases due to the low bioavailability
- The actual availability of heavy metals strongly increases due to decrease of the pH, which is caused by oxidation of FeS present in the sediment.

CONCLUSIONS

The practise of spreading of light contaminated sediments has not created large problems, due to the fact that most sediment are relatively clean and local background values are responsible for the soil quality. Local background values are often much higher than the natural levels. Negative effects are explainable (pH change) and consequently manageable. Model results shows that acceptance of spreading of more contaminated sediments (looking for the borders) may lead to decrease of the quality of agricultural land.

REMIEDIATING CONTAMINATED SITES IN NORTHERN CANADA

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INTRODUCTION

Indian and Northern Affairs Canada (INAC) is the custodian of a number of contaminated sites within the Territory of Nunavut. These sites are legacy sites that resulted from military activity, as well as mining and oil and gas exploration. In Nunavut, the majority of the high priority sites are from military activity that took place during the cold war era (1950s).

With the establishment of the Federal Contaminated Sites Action Plan (FCSAP) in 2003, funding was made available to remediate these sites. Throughout the cleanup of these sites we have encountered many challenges, some of which we were prepared for and others that we discovered along the way. Our office has successfully completed the cleanup of eight of these sites to date and work is underway at seven other sites.

This paper will discuss the challenges encountered while completing remediation work at sites in Nunavut, Canada, and the particular challenges associated with three sites: CAM-F Sarcpa Lake, FOX-C Ekalugad Fjord and Bear Island.

STANDARD CHALLENGES

Working in the north comes with some standard challenges that have to be met on nearly all projects. These include the weather, a short field season, remote locations, a lack of available services, regulatory issues, and land claim obligations. These challenges are always present but through proper planning their impacts can be minimized. To put things in perspective, the timeline to complete a project in Nunavut that requires 2 months of fieldwork is around 4 years. Needless to say a short delay can easily add another year, and significant costs to your project.

UNIQUE CHALLENGES

In addition to the standard challenges mentioned above, many of the contaminated sites we have worked on come with unique challenges. The following sections will discuss three individual projects, the challenges encountered, and how the project team dealt with them.

CAM-F Sarcpa Lake

The CAM-F Sarcpa Lake site presented a very unique challenge. This site is landlocked and as such required a two stage mobilization. The first stage involved mobilizing the equipment and materials from southern Canada via sealift. This began with the staging of equipment in Montreal in June/July. The sealift then carried the materials to Hall Beach (the community nearest to CAM-F). The sealift delivered the items in September and they were stored here until March when the second stage of the mobilization began. This involved moving the equipment and materials via CAT-Train overland to CAM-F. The site is approximately 80 km away from Hall Beach. During the CAT-Train we encountered further challenges with the design of the sleds and equipment problems due to the extreme weather.

FOX-C Ekalugad Fjord

The location of FOX-C on the northeast coast of Baffin Island contributed to the challenges associated with this site. Due to the location in the Fjord the site did not have an airstrip and the only to access the site was via sea or helicopter. The equipment and materials were mobilized via sealift but the crew changes and supplies were transported via helicopter,

which proved to be very costly. Also due to fog and other adverse weather we had a stretch of 12 days at site without a supply flight/crew change.

In addition to the mobilization challenges the specific characteristics of the site added more challenges. The camp/beach landing area were located at sea-level while the main station area was located approximately 750 metres above sea level. Due to this we had to construct a road to the upper site that climbed on average, 100 metres per kilometre. This road crossed a glacial stream a couple of times and in the first year we had a lot of rain at site which washed out the road. In the second year we had a lot of sun and due to the increased glacial melt the road washed out again.

Bear Island

The challenges at Bear Island began during the Phase III Environmental Assessment. Bear Island is a small island approximately 7.5 square kilometres in size and when we arrived to do the Phase III work we were greeted by seven resident polar bears. Luckily for us, five of the bears left the island and swam away, but one mother and cub stayed on the Island. To ensure employee safety we had bear monitors (experienced hunters) accompany the project team throughout the work. We were prepared for this when we returned to do the remedial works and had bear monitors monitoring all work crews and the camp 24 hours a day.

In addition to the bear challenge we also had regulatory issues that caused a one year delay and mobilization issues that cut our field season in half and stranded our equipment for an additional nine months.

CONCLUSIONS

This paper summarizes some of the challenges associated with remediating contaminated sites in northern Canada and also explores specific experiences gained on some sites. The goal is that through awareness and by sharing our experiences we can help others plan and successfully complete cleanup projects around the world.

REFERENCES

- Bliss, M., Nichol, R., Merkosky, R. (2011). Interim Remediation Completion Report, Bear Island, Nunavut. AECOM Canada Limited.
- Gilbertson, D., Schmidtke, R., Thompson, B., Yetman, M. (2007). Site Restoration Challenges at FOX-C. Fifth Biennial Workshop on Assessment and Remediation of Contaminated Sites in Arctic and Cold Climates.
- Labarge, S. Buchko, J., Yetman, M., Merkosky, R., Pelletier, J.P., Pouliot, Y. (2008). CAM-F Intermediate DEW Line Site Clean-up in Nunavut: From Procurement to Project Completion. Federal Contaminated Sites National Workshop 2008.

GROUNDWATER REMEDIATION IN NEWER VOLCANIC BASALT GEOLOGY: OPTIMISE THE EFFECTIVENESS OF ACTIVE REMEDIATION

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INTRODUCTION

It is always a challenge to optimise the effectiveness of any remediation technologies in the context of site specific conditions. Such conditions become even more important when we attempt to remediate in a complex geology and hydrogeology.

This paper discusses how the basaltic geology, depth to groundwater, groundwater hydraulic gradient, fractures, and velocity can affect the effectiveness of remediation.

METHODS

Several environmental investigations have previously been undertaken at the Site. The works involved the installation of 44 groundwater wells to assess potential contamination associated with historical Site activities. Sampling and analysis of the groundwater from these wells identified a number of contaminants, notably Light Non-Aqueous Phase Liquids (LNAPL), BTEX and chlorinated hydrocarbons (notably TCE, PCE, DCE and vinyl chloride) in an area in the south-west section of the Site.

RESULTS AND DISCUSSION

The concentrations of TCE indicated that Dense Non-Aqueous Phase Liquids (DNAPLs) may have been present in the aquifer, although none have been identified in groundwater monitoring wells.

The geology of the area consisted of Newer Volcanic basalts which constituted a fractured rock unconfined aquifer. The aquifer consisted of multiple basalt flows separated by interflow clay units of lower permeability than the basalt flows. The water table was located approximately one (1) metre above the first inter flow clay unit at approximately 7-8m depth.

Remediation of groundwater contamination in such a complex hydrogeological setting required a systematic approach; such an approach involved a comprehensive assessment of remediation options that lead to selecting technically feasible remediation technologies.

The next step was conducting field pilot trials on the most suitable methods to assess the technology efficacy in addressing the various contaminant types and development of a Remediation Action Plan (RAP). The refinement of how to apply the technology was a major objective of the trial. The remediation trials will be discussed in details and the outcome will be explained. The technology selection process involved assessing the technical effectiveness, logistical constraints and financial efficiency of each technology, which was subject to an independent review. The review indicated four (4) technologies for field trials:

- LNAPL baildown testing to assess LNAPL mobility and recoverability by fluid extraction methods (e.g. skimming);
- Multi-phase Vacuum Extraction (MPVE) to assess removal of volatile hydrocarbons;
- Soil vapour extraction (SVE) to assess removal of volatile hydrocarbons from the LNAPL; and
- In-Situ Chemical Oxidation (ISCO) to address the chlorinated hydrocarbon contamination in the aquifer.

The LNAPL bail down testing indicated the LNAPL was relatively mobile and, therefore, technologies relying on LNAPL mobility would be suitable remedial methods. These included skimming and MPE.

The SVE and MPE trials were conducted using the same extraction unit set up to extract vapours only (SVE) and total fluids plus vapours (MPE). The results indicated LNAPL recovery rates using MPE were in the order of 10 times that of SVE, hence demonstrating MPE was a more effective remedial method for LNAPL and would be suitable at the Site.

SVE was interpreted to be not suitable for remediation of LNAPL by volatilisation. However, the SVE trial did show a large (50m), albeit irregular, effective vacuum radius of influence – a result of the heterogeneous nature of the fracture systems in the basalt aquifer. The vacuum radius influence was a highlight of this method as it showed with a degree of clarity the extent of fracture in this unconfined basaltic aquifer. This site specific character is important on understanding the likely effectiveness of the selection of the remediation technology to be adopted.

Although the results of the ISCO trial were inconclusive with regards to TCE destruction, they indicated that injection of KMnO₄ solution into the aquifer was a feasible option. It also indicated the most appropriate injection rates required and the radius for the array of injection and monitoring wells for a larger scale remedial approach.

CONCLUSIONS

The development of remedial strategies for a complex fractured rock aquifer with varying types of contamination indicated the need for a systematic, staged and diverse approach. Amongst the benefits of such approach are cost effectiveness by testing the technologies at small scale, better understanding of remediation duration, refine the method of implementation.

REFERENCES

- American Standards for testing and Materials (2008) E 2531 – 06- Standard guide for development of conceptual site models and remediation strategies for Light Non-Aqueous Phase Liquid release to the substance.
- Lam, D., and Moritz, P. (2007) Impracticability of further remediation of LNAPL impacted soils and aquifers. CRC-CARE Technical report No. 6, CRC for contamination and remediation of the environment.
- ITRC (Interstate Technology & Regulatory Council) (2009) Evaluation LNAPL remedial technologies for achieving project goals. LNAPL-2. Washington D.C. ITRC LNAPL Team. www.itrcweb.org.

REMIEDIATING AND MANAGING RISK AT THE DUBBO BENZENE/MTBE PLUME

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INTRODUCTION

Historical leakage of petrol from an underground storage tank at a service station in Dubbo, NSW, resulted in a benzene plume in groundwater extending 560 m and an MTBE plume extending 1,140 m from the source. The aquifer is an important source for the town's water supplies and one town water extraction bore lay within the boundaries of the MTBE plume. This paper describes the process undertaken to define the plume behaviour, to determine plume stability and the measures taken to stabilise and remediate the benzene plume.

This work provides a case study in the management and remediation of a large scale benzene and MTBE plume that had impacted a critical beneficial use and potentially presented a health risk from vapour intrusion.

METHODS

Plume assessment

Delineation of the plume was considered complete after the installation of 75 monitoring wells and the plume's stability was established after 10 quarterly sampling rounds.

Health risk assessment

Two pathways for human health risk were considered and investigated – extraction of water for human consumption and potential vapour intrusion into residential dwellings. The former was mitigated by controls on the extraction of groundwater within the vicinity of the plume and the latter was investigated and the risk quantified by an extensive program of soil vapour profiling, flux measurements and indoor air testing.

Remediation strategy

The strategy chosen to control the further impact and migration of the plume and to enhance the rate of plume retardation, was to remove hydrocarbon mass from the plume, firstly by removing PSH and secondly by reducing the concentration of dissolved phase hydrocarbons. Removal of mass was considered an essential prerequisite to facilitate biodegradation and to initiate the commencement of the retardation of the plume.

Phase separated hydrocarbons (PSH) extending up to 120 m from the source, were removed by soil vapour extraction, initially using mobile units and subsequently an in-situ unit on site. Dissolved phase hydrocarbons were remediated by the injection of chemical oxidants. Immediately downstream of the extent of PSH, Regenox™ was injected at a series of wells along the plume axis and further down-gradient at two transects across the plume, 240 m and 370 m down-gradient of the source, ORC A™ a bioremediation enhancing oxidant, was injected.

Community consultation

In excess of 150 residences, lying either over the plume or in the vicinity, were contacted directly and advised of the planned investigations, remedial works and health risk assessment. Through personal contact and correspondence, residents were invited to discuss issues and concerns they may have, with Caltex directly.

RESULTS AND DISCUSSION

Plume assessment

The hydrocarbon plume lay in an unconfined aquifer within coarse alluvial gravels in a silty or sandy matrix at a depth of 16 m below ground level. Evaluation of the naturally occurring

bioattenuation indicators, nitrate, sulphate and ferrous iron, indicated that the plume was bioattenuating and quarterly monitoring events over three years showed the plume boundaries were stable. Plume age was estimated at 20-25 years.

Benzene was persistent over the plume's entire 560 m trajectory from the original petrol source while toluene had attenuated by 320 m and xylene also declined preferentially to benzene. MTBE was however, the most persistent compound, remaining in excess of the taste based US EPA drinking water criterion of 20 µg/L for a distance of 840 m.

Health risk assessment

An investigation program comprising multiple soil vapour concentration profiles, sub-slab measurements, indoor, crawl space and surface mass flux measurements confirmed vapour intrusion to be an incomplete pathway and thus, not a risk to the residents.

Remediation – removal of PSH

Soil vapour extraction by a mobile unit, utilising the extracted vapour stream to run the engines, removed an estimated 10,000 L of liquid hydrocarbon equivalent over 10 five day extraction events. A 'catox' soil vapour extraction unit constructed on-site, removed a further 20,000 L of liquid equivalent over a 16 month period.

Remediation – oxidation of dissolved phase

Still in the early stages of the oxidant injection program, large reductions in dissolved phase concentrations of hydrocarbons have been recorded in the vicinity of the injection wells.

Regulator Engagement

The investigation and remediation of this plume has been the subject of considerable regulator engagement with both the DECCW and the Dubbo City Council. Open communication between Caltex, the DECCW and the Council has facilitated the necessary off-site and on-site works and managed community expectations. Residents have recognised the willingness of, and the cooperation between Caltex and the authorities to address the risks and to remediate the plume, resulting in an effective remediation program.

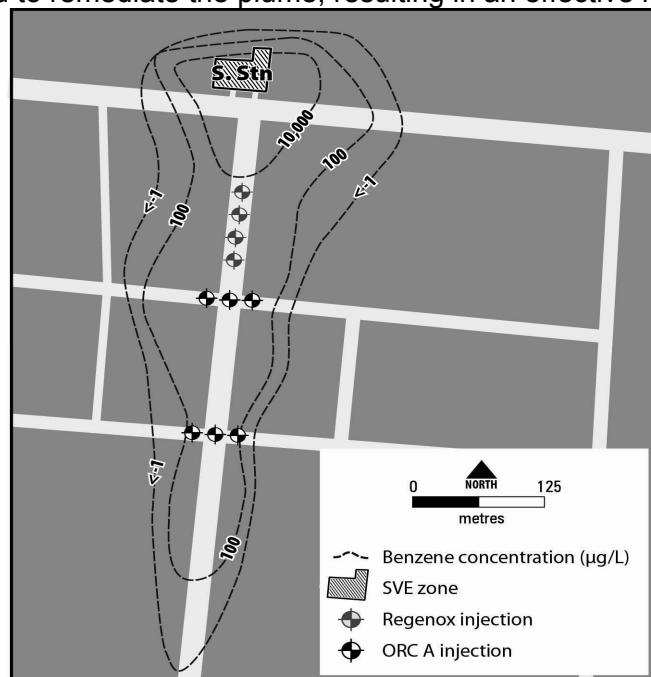


Fig. 1. Extent of the benzene plume, locations of soil vapour extraction and oxidant injection

CONCLUSIONS

Although of considerable age (20-25 years) and of large dimensions (benzene persisting 560 m from the source), the plume was shown to be stable and not advancing and naturally bioattenuating. Remediation by soil vapour extraction has essentially removed PSH previously extending up to 120 m from the source. Extensive vapour intrusion investigations have demonstrated that the vapour inhalation pathway is incomplete and not a risk to residents.

CHALLENGES OVERCOME DURING REMEDIATION OF THE BORAL BRICKWORKS SITE FOR RESIDENTIAL REDEVELOPMENT, WOONONA NSW

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INTRODUCTION

Remediation of the former brickworks site at Woonona commenced in 1998 and was completed in 2010, transforming the former industrial site to the Edgewood residential estate. Over 45 hectares of industrial land was remediated over the 13 year program and included soil remediation, groundwater and landfill gas investigations. Furthermore 11,300 m³ of asbestos impacted material was excavated, segregated and buried on-site.

The Edgewood Estate is located on the lower slopes of the Illawarra Escarpment, approximately 15 kilometres north of Wollongong. The site is underlain by shale and sandstone of the Illawarra Coal Measures that are typically exposed as a skeletal soil profile up to 15 metres thick. Groundwater at the site is located within the fractured bedrock sequence and is sometimes perched at the base of the weathered sequence.

The brickworks and kiln commenced operation in 1921 and continued operation until 1993 when the brickworks and industrial operations ceased. During the operations phase clay was quarried locally for brick making from two quarries to depths of up to 15 metres. As quarrying progressed soil, shale and clay not suitable for brick making was discarded across the site and was used to infill the quarries. Also buried with the waste raw materials was industrial waste including off-spec bricks, tyres, concrete and building rubble. In addition indiscriminate illegal dumping of household waste and building rubble (including asbestos) was emplaced in the two quarries during after industrial operations ceased.

The former brickworks site covers approximately 70 hectares of which 45 hectares are to be developed for a mixture of low density to medium density residential housing. Approximately 25 hectares that were not used for industrial purposes are to be managed as a green and golden frog habitat and riparian corridors under community title.

METHODOLOGY

The remediation program was undertaken in accordance with the NSW DECCW guidelines for contaminated sites. 24 technical reports and 18 site audit reports were prepared in accordance with the NSW DECCW site auditor scheme to support the residential development. Initially a hydrogeological investigation was conducted to characterise groundwater across the whole site. Site investigation and soil validation investigations were then staged across the site as access became available. Individual development stages varied in size between one and three hectares with individual investigation scope and validation methodologies developed based on the site history and site characteristics.

The chemicals of concern across the site were hydrocarbons TPH (total petroleum hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylene), polychlorinated biphenyls (PCB), organochlorine pesticides (OCP), asbestos and heavy metals (As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn). In early investigations soil samples from similar lithologies were composited for metals analyses, however this methodology was discontinued after changes in the DECCW guidelines.

The majority of site infrastructure including building and underground storage tanks was removed in the mid 1990s. Hydrocarbon impacted areas were excavated and contaminated soil was land farmed on site. Site investigations were conducted using targeted sampling

where contamination was known or suspected and an evenly spaced random sample pattern with the sample density selected in accordance with NSW EPA Sampling Design Guidelines.

Lithological samples were collected from different soil or fill horizons and submitted for laboratory analysis routinely for heavy metals and randomly and/or targeted for hydrocarbons, pesticides and asbestos. Gas monitoring wells were installed in the eastern quarry to monitor the potential for methane due to the presence of putrescible waste. Following the completion of soil validation investigations the soils and fill were excavated to bedrock by the earth works contractors and foreign materials removed before reinstatement. In 2006 a 1.7 hectare industrial site formerly used for boat building was added to the estate and consequently tributyl tin was included as a potential contaminant of concern.

RESULTS AND DISCUSSION

Throughout the thirteen year soil investigation and validation program many challenges were faced. Over 1000 metals analyses were conducted across the site and the exceedences were within statistical variation limits. Foreign objects isolated from the fill were segregated and sorted and recycled where possible. Bricks and concrete was crushed and used as road base and steel and tyres were recycled off-site.

In 2001 the green and gold bell frog was identified in the Southern Pit halting further development until the frog's breeding habits could be studied and the frogs relocated to a purpose built frog habitat containing shelters and six ponds. In January 2007 access to the former Southern Pit was granted but the discovery of fragments of bonded asbestos cement sheeting (fibro) within some of the clay fill initiated an asbestos segregation program. A total of 11,300 m³ of asbestos impacted material was temporarily stockpiled within the quarry.

Asbestos disposal options were off-site disposal or on-site burial and encapsulation. Off-site disposal in existing landfill was expensive and not considered an appropriate environmental option. In 2008 following legislative changes to the *POEO Act, 1997* and discussions with Wollongong Council and site auditors the asbestos impacted material was buried within a 12 metre deep trench constructed beneath a 30 metre wide corridor along the southern Estate boundary. The asbestos was encapsulated beneath a geofabric layer, a sand marker bed and a minimum two metres of clay.

In addition the 30 metre wide open space corridor serves the dual purpose of providing a purpose built frog translocation corridor linking the public reserve and Farrahars Creek with the frog habitat to the west and as a floodway. A dedicated overland flow path and pipe beneath the corridor was designed to direct flow across the site into Farrahars Creek. The open space corridor is managed under an Asbestos Management Plan for the ongoing management of enclosed asbestos impacted soil.

CONCLUSIONS

Despite the site being used for industrial activities for over 70 years the hydrocarbon contamination was limited to around some underground storage tanks and near the kiln. Furthermore there were virtually no heavy metals or pesticide contamination across the site. The majority of site contamination was associated with discarded quarry waste within clay and soil not suitable for brick making and indiscriminate dumping of building rubble and household waste after quarry operations had ceased.

An innovative solution was to dispose of 11,300 m³ of asbestos impacted material on-site within a trench and encapsulation beneath an open space corridor which served as a frog translocation corridor and an overland flow path for storm water. The remediation program and development successfully transformed a contaminated industrial site into a desirable residential location. During the development the natural environment was enhanced as the quarries were infilled, the industrial land re contoured, ponds created and creeks diverted to and public open space was created.

MEAD STREET, BIRKENHEAD – RESIDENTIAL FUTURE FOR GASWORKS SITE POSES CHALLENGES FOR AUDITOR

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INTRODUCTION AND BACKGROUND

In 2006 the Department for Families and Communities (DFC) engaged Adrian Hall to conduct a site contamination audit for a former gasworks site located at 75 Mead Street, Birkenhead SA. Originally owned by the SA Gas Company, the site was historically used as a works depot and contained a gasometer for the storage of gas. In the early 1980s the site was purchased by a private company and developed for housing. The South Australian Housing Trust subsequently purchased the 16 completed residential units in August 1982. Following complaints about odours, soils investigations undertaken within the front and back yards of each of the units detected the presence of 'gasworks waste', characterised by elevated concentrations of PAHs throughout the site, either in a discrete band or distributed within the near surface soils. During those investigations DFC, on advice from the SA Health Department, commenced the evacuation and relocation of all tenants from the site. The relocations were completed and the site fenced off by July 2003. At the same time groundwater investigations were commenced both on site and off site.

AUDIT PROCESS

The audit has involved the review of further soil and groundwater investigations undertaken by Golder Associates, and a Remediation Management Plan (RMP). Remediation was designed to be achieved by excavation of all PAH contaminated soils, and treatment of the highly impacted soils off site at the recently commissioned facility at Integrated Waste Services (IWS), Dublin. Following the completion of remediation works, it was envisaged that the auditor would provide a 'Remediation to the Extent Necessary' (RTEN) opinion, in accordance with the EPA (2009) Guidelines for the Assessment and Remediation of Groundwater. The audit has been conducted by Adrian Hall, assisted by Jean-Paul Pearce.

SOIL REMEDIATION WORKS

Soil remediation works undertaken by the contractor, McMahon Services commenced in October 2010 and were completed in February 2011. Works included:

- (a) Excavation, stockpiling and classification of excavated materials on site;
- (b) Haulage and off-site treatment and disposal of 'high level' contaminated soils;
- (c) Cut-to-fill earthworks using natural soils and imported clean fill; and
- (d) Backfilling excavations with compacted fill to restore natural site levels.

Some 2,000 tonnes of soils were classified as 'high level' contaminated soil due to elevated concentrations of PAHs, particularly benzo(a)pyrene. These soils were transported to the IWS Multipurpose Waste Treatment Facility (MWTF) at Dublin, where they were successfully treated using an EPA-approved chemical immobilisation and solidification method. Other materials were classified as 'low level' contaminated soil, or 'intermediate' landfill cover, and transported to appropriately licensed facilities for disposal.

MANAGEMENT OF DUST AND ODOUR EMISSIONS

Due to the nature of the site contamination it was assumed that any dust leaving site was contaminated, and therefore every effort was made to ensure that dust generation was minimised. 'Dust Trak' monitors were used provide real-time monitoring of dust emission, in conjunction with an on-site weather station to ensure appropriate placement and use. As this

was considered to be a key issue for the protection of the community during the remediation works, this issue needed to be closely managed by the remediation contractor.

Odour emissions from the site also presented a key issue to the community and needed to be carefully managed. PID monitoring was undertaken near the excavation face together with perimeter monitoring, and the contractor used excavation techniques for the 'high level' contaminated soil designed to minimise odour generation. In addition the contractor used odour suppressant misting sprays at the downwind excavation face and on the downwind site boundaries. Since odour is an aesthetic issue (which a PID cannot measure), perimeter monitoring (by smelling) was regularly undertaken by non-site personnel, who would not be subject to de-sensitisation.

GROUNDWATER INVESTIGATIONS AND RTEN OPINION

Groundwater contamination, principally by cyanide, was identified on site and extending off site in a north-easterly direction. The contamination appeared to be from a combination of site-derived and off-site sources, and based on the results of Groundwater Monitoring Events (GMEs) undertaken between 2003 and 2010, the full extent of groundwater contamination remained undefined. The EPA (2009) groundwater guidelines required a Detailed Risk Assessment (DRA) to be prepared, and an RTEN opinion to be provided by the auditor for inclusion into the Site Contamination Audit Report (SCAR).

One of the challenges of this audit was assigning responsibility for groundwater contamination. Section 103C of the Environment Protection Act defines the 'appropriate person' who can be issued with a site contamination assessment or site remediation order; however where necessary the EPA can make a determination as to whether or not a person is an 'appropriate person'. For the Mead Street site, where the person (i.e. DFC) was the owner of the source site, but did not cause the contamination, that person was considered to have liability for the contamination, but the liability would be limited to the boundaries of the actual site. In this case the EPA required the owner to undertake assessment and necessary remediation, but only within the site boundaries. The auditor was required to consider the groundwater contamination at the site insofar as it affected the site itself, and also to consider the potential impact the contamination might have if it continued to migrate outside the site boundaries. The auditor was not required to consider the nature or extent of the groundwater contamination off site; this issue was to be addressed separately by the EPA in consultation with DFC.

CONCLUSIONS

The site contamination audit process is well defined in the legislation, but needs to be a balance between the regulatory requirements, the science upon which the legislation is based, and ultimately the health and wellbeing of the people of South Australia and the environment. As the Mead Street site illustrates, it is only through open communication between the auditor, the client, the assessing consultant, the remediation contractor and the regulator that the audit can be completed in an effective and efficient manner.

REFERENCES

- EPA South Australia (2008a), *Guidelines for Environmental Management of On-site Remediation*, November 2008.
- EPA South Australia (2009b), *Site Contamination, Guidelines for the Assessment and Remediation of Groundwater Contamination*, February 2009.
- South Australia (1993), *Environment Protection Act 1993*.

LIME ASSISTED TIDAL EXCHANGE AS A LOW COST TECHNOLOGY FOR BROAD-SCALE ACID SULFATE SOIL REMEDICATION

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Acid sulfate soils (ASS) are soils containing iron sulfides, commonly pyrite. When exposed to air due to drainage or disturbance these soils produce sulfuric acid, often releasing toxic quantities of iron, aluminium and heavy metals. ASS are a serious issue in coastal areas around Australia and account for an estimated 40 million hectares worldwide. This study has assessed the use of lime-amended tidal exchange to remediate an iconic acid sulfate soil site, East Trinity, near Cairns, Northern Queensland. The acid sulfate soil impacts at East Trinity began in the 1970s, when developers installed a 7 km long seawall, tidal gates, drained and cleared 740 hectares of tidal wetland to grow sugarcane. This dried out underlying acid sulfate soils (ASS) causing them to release slugs of highly acidic water as low as pH 2.5, causing fish kills and destruction of wetlands. In the first 25 years following this land development, an estimated 72,000 tonnes of sulfuric acid was released into Trinity Inlet.

The remediation of East Trinity has involved broad-scale soil and drainage works to complete a fully operational Lime Assisted Tidal Exchange management system. The system uses new-technology floodgates and lime dosing to control the exchange of tidal waters into the wetland drainage system, partially restoring marine tidal inundation. Five years of regular tidal inundation has led to substantial improvements in soil and water quality. Continuous monitoring shows that discharge water is being maintained above the target pH 6, and soil geochemistry is changing dramatically in favour of reductive, acid-consuming geochemical processes. Inundation by seawater has triggered anoxic reductive dissolution and redistribution of iron in this landscape. Porewater Fe^{II} concentration exceeds 30 mM at the inundation front, and surface accumulations of Fe oxides in the most recently inundated parts of the landscape are typically between 2- 20 cm thick. Microbial-mediated reduction of the iron and sulfur is resulting in the progressive formation of iron sulfide minerals (mostly pyrite) and beneficial effects of in situ alkalinity generation. In response, Soil pH has increased by 2-3 units and titratable actual acidity decreasing by ~50 $\mu\text{mol H}^+ \text{g}^{-1}$ within the former sulfuric horizons. The cost of restoration to date has been around \$10 million – a fraction of the estimated \$300 million it would have cost to neutralise the soils by conventional means. This study has established East Trinity as a National Demonstration Site for Innovative Acid Sulfate Soil (ASS).

SYNTHESIS, CHARACTERIZATION AND ENVIRONMENTAL APPLICATIONS OF IRON-BASED NANOPARTICLES

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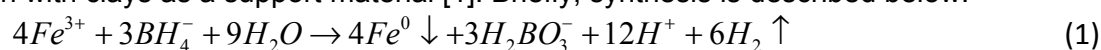
INTRODUCTION

Nanoscale zero-valent iron (nZVI) represents the most widely studied engineered nanomaterial in environmental remediation and toxic waste treatment [1]. However, nZVI's intrinsic structure may limit its reaction rate. Decreasing iron reactivity is observed over time due to the formation of oxide layers on the particle surface during the reaction, or upon contact of the nZVI particles with air. To enhance the reactivity and functionality of nZVI particles, nZVI can be impregnated with a second metal such as Pd, Pt, Ni and Ag to form bimetallic nanoparticles [1]. However, the aggregation of nanoparticles results in the decrease of reactivity. Hence, subsequent efforts to reduce the aggregation of nanoparticles have led to synthesizing supported nanoparticles. In this presentation, we summarized our recent work based on iron-based nanoparticles, where clays as a solid support for immobilization of Fe or Fe/Pd nanoparticles. Iron/ Pd nanomaterials were synthesized, characterized and used for the remediation of contaminants since clay is a low-cost and efficient adsorbent because of its abundance, chemical and mechanical stability, high adsorption capability and unique structural properties [1].

METHODS

Synthesis of supported Fe and Fe/Pd nanoparticles

Clay-supported Fe/Pd (B/Fe/Pd) nanoparticles were synthesized using liquid-phase reduction with clays as a support material [1]. Briefly, synthesis is described below:



The synthetic reaction occurs in the following way:



All the prepared samples were dried at 60°C under vacuum overnight, and kept in a nitrogen atmosphere prior to use.

RESULTS AND DISCUSSION

1. Kaolinite-supported nanoscale zero-valent

Three adsorbents (kaolin, nZVI and K-nZVI) were used to remove Pb^{2+} from aqueous solution. As shown in Fig.1, 96.7% of Pb^{2+} was removed using K-nZVI, only 5.8% and 16.8% of Pb^{2+} was removed using kaolin and nZVI, respectively. When using K-nZVI, equilibrium was reached after 10 min while 20 min was required when employing either kaolin or nZVI. This indicated that the rate of removal of Pb^{2+} from solution using K-nZVI was much higher than that of either kaolin or nZVI. The reason for this is that, as a support material, kaolin could stabilize and disperse nZVI as well as prevent nZVI from aggregation, which was confirmed by SEM (Fig.2). The results showed that 99% of Pb(II), 99.8% of total Cr(VI) 69.5% of Cu(II), 28.1% of Zn(II) and 23.0% of Ni(II) were removed from an electroplating wastewater .

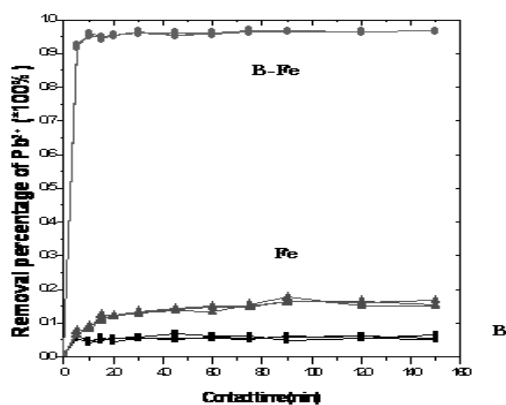


Fig1. Removal in percentage of Pb²⁺

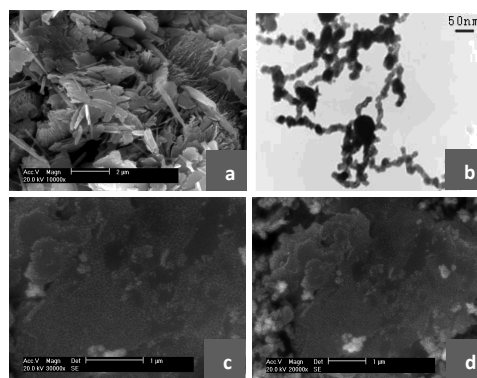


Fig.2 SEM. (a) kaolin; (b) nZVI; (c) and (d) K-nZVI.

2. Bentonite-supported Fe/Pd nanoparticles

Figure 3 shows the dechlorination of p-chlorophenol (p-CP) using bentonite, B/Fe, Fe/Pd and B/Fe/Pd. 100% of p-CP was removed from solution within the first 90 min using B/Fe/Pd and 120 min using Fe/Pd, while only 25.0% and 15.0% was obtained using B/Fe and bentonite after 180 min, respectively. This indicates that the bentonite can enhance the reactivity of Fe/Pd, and the dechlorination rate of p-CP. B/Fe/Pd was much higher than that of B/Fe due to the fact that Pd as a catalyst plays a role in hydrogen formation, activation, and the subsequent formation of dissociated hydrogen species [1]. In contrast, a low removal efficiency was obtained using B/Fe, which can be explained by the corrosion of B/Fe, leading to rapid formation of surface-passivating oxide layers due to its large surface area [23]. These oxide layers blocked the active sites on the surface of B/Fe, and hence, inhibited the direct electron transfer from the iron surface to p-CP [1]. This was confirmed by XRD (Fig. 4).

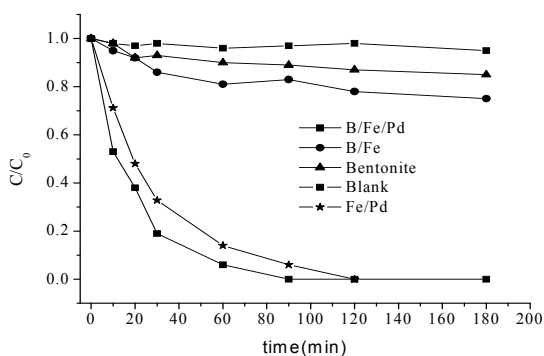


Fig.3. p-CP removal using various materials

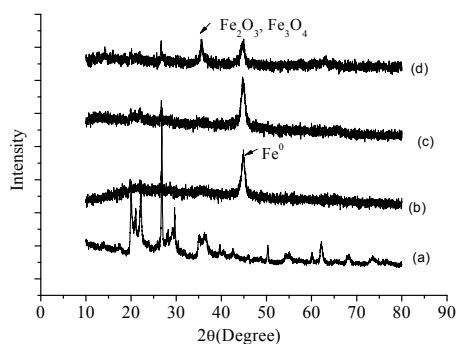


Fig.4. a. B; b. B/Fe; c. B/Fe/Pd; d. B/Fe/Pd

CONCLUSIONS

Clay supported iron-based nanoparticles can be used for the sorption/ degradation of inorganic and organic contaminants. Clay as the support material led to increased dispersion of Fe/Pd nanoparticles in of and reactivity was improved. Additionally, the formation of oxide layers on the nanoparticle surface can be improved by impregnation with a second metals.

REFERENCES

Theron J, Walker J A, Cloete, TE (2008) Nanotechnology and water treatment: applications and emerging opportunities, Crit. Rev.in Microbio, 34, 43-69.

MULTI-TECHNIQUE APPROACH TO THE CHARACTERISATION OF ENGINEERED NANOPARTICLES

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INTRODUCTION

As applications of nanomaterials are growing rapidly, the ability to determine the impact of engineered nanoparticles (ENPs) on the environment, health and workplace safety is becoming more important. One of the main challenges is to accurately characterize physical and chemical properties of ENPs such as particle size, surface area, number concentration, agglomeration/aggregation state, surface charge, and chemical composition. Accurate measurements of dimensional properties such as particle size are of fundamental importance for the understanding and control of the characteristics of nanomaterials since size is often strongly correlated with properties that determine the interactions with biological systems.

In this study we have used mono-and multi-modal dispersions of nanoparticle reference materials to compare and contrast the average particle size and particle size distribution measured by a number of different techniques, including transmission electron microscopy (TEM), dynamic light scattering (DLS), differential centrifugal sedimentation (DCS), nanoparticle tracking analysis (NTA) and a new technique based on a micro-channel resonator (MCR) which provides ultra high-resolution mass sensing.

PARTICLE SIZING MEASURANDS – WHAT IS BEING MEASURED?

Whilst “particle size” appears to be a straightforward parameter, in reality particle systems are quite complex, comprising broad or multimodal size distributions, often with shape inhomogeneity, which can not easily be represented by a single number.

Care is also required when comparing results from different particle characterization techniques since these may be based on different measurands. For example, DLS determines the average hydrodynamic diameter of a particle ensemble while TEM determines particle dimensions based on the projection of the particle outline onto a two-dimensional image plane.

COMPARISON OF PARTICLE SIZING TECHNIQUES

A variety of methods have been developed to measure the dimensional properties of nanoparticle systems. Ensemble techniques such as DLS average over a large number of particles and provide a good statistical representation of the sample properties, but may not be suitable for samples characterized by wide distributions of particle size or shape (Jämting *et al.*, 2011). Single-particle resolution techniques such as TEM or atomic force microscopy can provide detailed information on particle size and shape but may be hampered by limited statistical relevance due to the relatively small fraction of particles examined. Separation and classification techniques such as DCS, liquid chromatography and field flow fractionation overcome some of these limitations by presenting smaller particle ensembles corresponding to sub-sets of the size distribution to the detection and measurement systems sequentially. Increasingly, these techniques are being complemented by novel methods such as NTA and MCR which can achieve single-particle resolution at moderate throughputs to obtain statistically representative information on sample characteristics while maintaining high resolution.

Example 1: Comparison of DCS with DLS

Due to the non-linear dependence of scattered light intensity on particle size, DLS measurements can be strongly influenced by the presence of larger particles in the sample.

Size classification techniques such as DCS overcome some of the limitations of DLS for the characterisation of samples with broad size distributions, as illustrated in Figure 1 below. The resolving power of DCS allows the detection of agglomerate clusters, in this case of polystyrene latex particles, including doublets, different conformations of triplets, quadruplets etc as indicated in the main panel of Figure 1. In comparison, DLS (inset of Figure 1) returns an inadequate representation of the particle size distribution because scattering from larger agglomerate clusters dominates the signal.

Example 2: Comparison of DCS with MCR and DLS

A mixture of three aqueous suspensions of gold nanoparticles with nominal diameters of 56, 79 and 99 nm was used to compare the DCS, MCR and DLS techniques. The main panel of Figure 2 illustrates that both DCS and MCR are capable of resolving all three peaks of the size distribution. The peak positions coincide, with the exception of the peak near 50 nm which is at the detection limit for the MCR resonator, so it is likely that the complete peak is not detected. As shown in the inset of Figure 2, DLS is unable to resolve the three different populations present and returns a size distribution that is not representative of the sample.

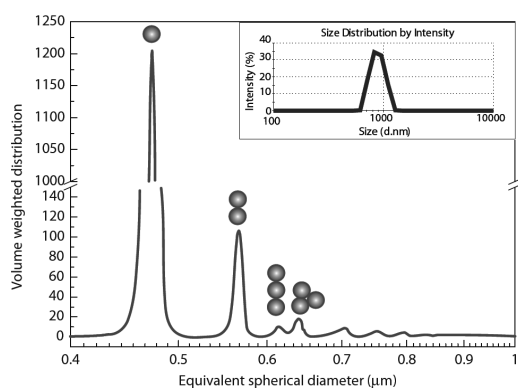


Fig. 1. Comparison of the volume weighted particle size distributions measured by DCS (main panel) and DLS (inset) for an aqueous suspension of polystyrene latex particles with a nominal diameter of 460 nm (Sigma Aldrich) which has undergone agglomeration.

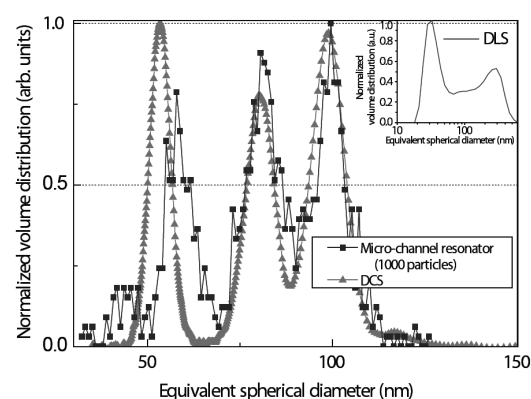


Fig. 2. Comparison of the volume weighted particle size distributions measured by DCS (triangles), MCR (squares) and DLS (inset) for a tri-modal aqueous suspension of gold nanoparticles with nominal diameters of 56 nm (NIST RM 8013), 79 and 99 nm (BBI International).

CONCLUSIONS

To determine the impact of nanoparticles on the environment, reliable characterisation of the particle properties is fundamental. In this study, four different particle sizing techniques were compared and contrasted using a number of different particle systems with well-controlled properties. Whilst DLS and TEM are commonly used, they have significant draw-backs: obtaining average particle sizes and size distributions by TEM is labour- and time-intensive, whilst DLS often fails to accurately represent samples that do not have narrow size distributions. DCS and MCR are attractive alternative particle sizing techniques offering high-resolution sizing with relatively short acquisition and analysis times.

REFERENCES

- Jamting, Å. K., Cullen, J., Coleman, V. A., Lawn, M., Herrmann, J., Miles, J., Ford, M. J. (2011) Systematic study of bimodal suspensions of latex nanoparticles using dynamic light scattering. *Adv. Powder Technol.* 22: 290–293.
<http://www.sigmaldrich.com>. Accessed on 15 April 2011.
https://www-s.nist.gov/srmors/view_detail.cfm?srm=8013. Accessed on 15 April 2011.
<http://www.bbigold.com>. Accessed on 15 April 2011.

NANOTECHNOLOGY: ENVIRONMENTAL APPLICATIONS AND IMPLICATIONS

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Nanotechnology involves research, development, control, and characterization of materials or devices between the atomic and micrometer scales (usually in the 0.1–100 nm range). Nanomaterials (NMs, materials that contain nanoparticles, NPs) exhibit novel properties that differ from those of bulk materials due to the interactions and physics between atoms. Because of their unique properties, NMs have been used in many different sectors for all kinds of purposes. Currently, environmental applications of nanotechnologies provide new opportunities for us to detect, control, and remediate environmental pollutions. However, as with any new technology or chemical substance, there is a potential for harm to human and natural ecosystems from nanotechnology. For these reasons, research related to environmental nanotechnology mainly focus on two major directions: (a) synthesizing new NMs (e.g., magnetic NMs or nanomembranes) or developing new techniques (e.g., nanosensors) for enhanced environmental protection; and (b) defining the problems and processes that might occur in the two ecosystems by evaluating the environmental and economic benefits/risks of new nanotechnologies. Since the 1990s, studies in both directions have generated enough information. It would be beneficial to review these studies within the frame of applications and implications of nanotechnology.

In this presentation, the state-of-the-art environmental applications of nanotechnology will be introduced, such as a) pollution control or contaminant remediation with nanoscale zero-valent iron (NZVI) particles, NZVI encapsulated in biodegradable calcium alginate capsules, carbon onion nanoparticles, and TiO₂ nanoparticles; b) development of nanosensors for detection of emerging contaminants; c) nanomembranes for water/wastewater treatment and gas/liquid separation and CO₂ sequestration/storage. Surface functionalization and modification of NMs with unique functional chemicals or polymers would greatly extend potential for new applications of NMs. To evaluate implications of nanotechnology, this presentation will focus on NM-induced characteristics, interactions and behaviours. Stability of NMs under different conditions and in different compartments will be discussed. Effects of NMs on host organisms will be evaluated, including a) irrecoverable damage to the host organisms by physical damage to the outer membrane of the cells, b) overload on phagocytes (cells that ingest and destroy foreign matter) that may trigger stress reactions, and c) sorption into tissues that may affect the regulatory mechanisms of enzymes.

In summary, the stability of NMs and methods used to manipulate surface chemistry/components for control of aggregation, surface coatings, and bonded surface species are important and still will be the future directions. In addition, it is imperative to do more research on fate of NMs, NM-induced characteristics, and corresponding interactions and behaviours of NM in water environments.

CLOSING THE GAP IN ENVIRONMENTAL RISK ASSESSMENT OF NANOMATERIALS THROUGH INTERDISCIPLINARY METHOD DEVELOPMENT

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INTRODUCTION

Over the past decade, rapid innovation and commercialisation in the field of nanotechnology has ensured continuous growth in this sector (e.g. Meyer et al., 2009). As a result, an increasing number of manufactured nanomaterials (defined as engineered particles with at least one dimension <100 nm) have been incorporated into products and manufacturing processes. This growth has been met with an equivalent increase in concern regarding the safety of manufactured nanoparticles with respect to human and environmental health. This is because, as with most products of human activities, their intentional or accidental release to the environment is largely unavoidable (e.g. Colvin 2003; Grieger et al., 2009). In response to this increasing cause for concern, the scientific community has begun investigating the environmental consequences of nanotechnologies. Some studies have shown that physico-chemical parameters of the nanomaterials, such as size and surface charge, can significantly influence their toxicity (e.g. Pal et al., 2007).

Yet despite efforts on the part of ecotoxicologists, risk assessment of both existing and emerging nanotechnology lags significantly behind commercial developments (e.g. Ju-Nam and Lead, 2008). This knowledge gap is an issue not only in terms of environmental legislation but also for the sustainability of the industry as public perception plays an important role in the acceptance of new technologies. The growing divergence between risk assessment and commercialisation is underlain by two key factors. Firstly, significant methodological and analytical challenges hinder the meaningful study of nanoparticles in complex environmental media; and secondly, insufficient interdisciplinary collaboration between nanotechnologists and environmental scientists has stymied environmental research in this field.

The main aim of this research is to close the gap between innovation in nanotechnology and environmental nanoscience by:

- a) Designing and producing commercially relevant nanoparticles optimised for environmental risk assessment;
- b) Developing new methodologies based on isotopic techniques and *in situ* advanced spectroscopy

METHODS

Arguably the most common approach to environmental risk assessment of nanomaterials is based on the testing of commercially available 'off-the-shelf' materials. This approach is understandable as it is convenient and deals with commercially relevant products but it also has considerable shortcomings:

- a) It is virtually impossible to obtain functionalised commercial nanomaterials with comparable core structure in terms of size and composition; and

b) It precludes the possibility of using isotopic tracing techniques for assessing environmental resilience.

In this research nanomaterials are synthesized using either stable or radioactive isotopes. This will allow the development of isotopic techniques for tracing the fate of the metallic components during experiments.

A further key challenge in the risk assessment of nanomaterials is related to the difficulty in quantifying nanomaterials once they are dispersed in complex environmental matrices. This endeavour can truly be described as trying to find the proverbial 'needle in a haystack'. To overcome this issue, nanoparticles will be immobilized on surfaces. Nanoparticles deposited on surfaces will be then be exposed to environmental media such as raw wastewaters, wastewater digestate, and natural waters.

Finally, the potential of direct assessment of nanomaterials based on *in situ* chemical fingerprinting using spectroscopic techniques will be explored.

RESULTS AND DISCUSSION

This presentation will cover the key results of this recently started project. It is expected that the project will deliver essential information that is urgently required to determine the potential environmental risk posed by nanoparticles which are very heavily employed in commercial products. Secondly, at a higher level, the project will deliver outcomes in relation to new methodologies and a new risk assessment framework based on surface functionality. Both the methodologies and the framework will provide the foundation for the risk assessment of other nanomaterials.

REFERENCES

- Colvin VL (2003) The potential environmental impact of engineered nanomaterials. *Nature Biotechnology* 21(10), 1166-1170.
- Grieger KD, Hansen SF, Baun A (2009) The known unknowns of nanomaterials: Describing and characterizing uncertainty within environmental, health and safety risks. *Nanotoxicology* 3(3), 1-U17.
- Ju-Nam, Y., and Lead, J.R. (2008). Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of the Total Environment*. 400:396-414.
- Meyer DE, Curran MA, Gonzalez MA (2009) An Examination of Existing Data for the Industrial Manufacture and Use of Nanocomponents and Their Role in the Life Cycle Impact of Nanoproducts. *Environmental Science & Technology* 43(5), 1256-1263.
- Pal S, Tak YK, Song JM (2007) Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticles? A study of gram-negative bacterium *E. coli*. *Applied Environmental Microbiology*. 73: 1712-1720.

APPLICATION OF MAGNETIC NANO/MICRO SCALE IRON-BASED PARTICLES ON WASTEWATER TREATMENT AND SOIL/GROUNDWATER REMEDIATION: EFFECTIVENESS, REGENERATION AND CHALLENGES

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Nanoparticles are attractive to many researchers because they are effective for metal and organic removal due to their large surface area to volume ratio and greater number of reactive sites. Magnetic nanoparticles (MNPs) are the advanced development of nanoparticles because of its added-value of magnetic properties, which enhance their wide-ranging applications of environmental remediation. Two common methods, such as coprecipitation and sol-gel, have been developed for synthesizing MNPs with different iron compositions (such as $\gamma\text{-Fe}_2\text{O}_3$, MeFe_2O_4 , and metal-doped $\gamma\text{-Fe}_2\text{O}_3$). The preparation of magnetic nanoscale iron-based particles is safe, simple, and inexpensive. Characterizations of the magnetic nanoparticles can be carried out using X-ray diffractometer (XRD) for crystal identification, transmission electron microscopy (TEM) for size and morphology investigation, BET method for surface area measurement, and vibrating sample magnetometer (VSM) for magnetic behavior analysis.

The application of MNPs for the removal of toxic metals and organics in contaminated water has also been demonstrated. After wastewater and groundwater treatment, the recovery of MNPs by the magnetic separation technique makes its potential to achieve complex environmental separations. Additionally, magnetically activated nanoparticles can be used as passive environmental adsorbents that can be placed in the subsurface environment and at river bottoms. These adsorbents can subsequently be retrieved and separated from the groundwater and the sediments through the application of a magnetic field, and then regenerated. Apparently, the magnetic nanoparticles possess the advantages of large surface area, high number of surface active sites, and high magnetic properties, which lead to high adsorption efficiency, high removal rate of contaminants, and easy and rapid separation of adsorbent from solution via magnetic field. However, on the subject of the recovery and regeneration of spent nanoparticles, little field information is available because of their difficulties of applying magnetic field in real application. The efficiency of magnetic separation is a function of the size of nanoparticles and the applied magnetic field, and thus a trade-off between the particle size and the technically feasible magnetic field should be of consideration.

Besides recovery and regeneration issues, it is crucial to chemically stabilize the morphology and magnetism of MNPs during and after synthesis, in order to prevent their agglomeration, and to keep MNPs from being oxidized. In addition, toxicity of nanoparticles has been found to be related to their types and reactions occurring in the bacteria cells. Dissolution of spinel phases is a matter of great practical importance related to corrosion science, surface science, and crystal growth technology. Factors affecting dissolution involves the composition of the solution phase and the physiochemical properties of the MNPs.

The promising application of nanoparticles for *in situ* treatment via direct injection into a contaminated zone has been reported. However, the fate and transport of contaminants immobilized with nanoparticles become an environmental concern. Unfortunately, there has not been any report in this regard so far. It has been found that under certain subsurface conditions the transport of nanoparticles can be greatly enhanced, leading to widespread contamination if there are contaminants associated with these nanoparticles. Therefore, assessing the fate and transport of nanoparticles in environmental media deserves much research attention because this is a key component of exposure and risk assessment of this nanotechnology.

In this presentation, the focus would be on the environmental application of MNPs, their effectiveness and removal mechanisms, the challenges being faced for industrial applications, potential solutions for solving the technical problems as well as future development of the MNPs.

BIOSYNTHESIS OF IRON AND SILVER NANOPARTICLES AT ROOM TEMPERATURE USING AQUEOUS SORGHUM BRAN EXTRACTS

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INTRODUCTION

Metallic and metal oxide nanomaterials have attracted tremendous interest due to their unique physicochemical and optoelectronic properties. Nanoparticles of specific sizes and morphologies can be readily synthesized using chemical and physical methods. However, these methods employ toxic chemicals as reducing agents, organic solvents, or nonbiodegradable stabilizing agents and are therefore potentially dangerous to the environment and biological systems (Nadagouda et al., 2009). Biosynthesis of nanoparticles using plant materials has been proposed as a cost-effective environmental friendly alternative to chemical and physical methods. Although the synthesis of metallic and metal oxide nanoparticles using plant materials has been demonstrated (Chandran et al., 2006; Nadagouda et al., 2010; Jha et al., 2009), a rapid, cost-effective biosynthetic protocol for bulk synthesis of stable nanoparticles has not been developed. Such a method is important for the full potential of these nanomaterials in environmental remediation and other technological applications to be realized. In this study, the biosynthesis of iron and silver using aqueous hybrid sorghum (*Sorghum* spp) bran extracts was investigated. The performance of the synthesized iron nanoparticles in the H₂O₂-catalyzed degradation of organic contaminants was also studied using bromothymol blue (BTB) as a model organic contaminant.

METHODS

Specialty sorghum bran (*Sorghum* spp) powder was obtained from VeruTEK Technologies Inc. (Bloomfield, CT, USA). The sorghum powder (8.3 g) was extracted with 125 mL of distilled deionized water (DDW) at 25, 50, and 80°C while being continuously stirred for 30 min. Samples were then centrifuged at 8000 rpm for 30 min and the resultant supernatant collected, filtered, and stored at -20°C. The total phenolic content of the aqueous extracts was determined by the Folin-Ciocalteu method using gallic acid as a standard phenolic compound as described by Slinkard and Singleton (Slinkard and Singleton, 1977). Iron nanoparticles were prepared by adding 0.1 M FeCl₃ solution to the sorghum bran extract (supernatant at ambient temperature) in a 2:1 volume ratio. The mixture was hand shaken for 1 min and allowed to stand at room temperature for 1 h. The same procedure was used to synthesize silver nanoparticles using 0.1 M AgNO₃ solution. Samples were characterized using FE-SEM, HR-TEM, XRD, EDS, and UV-Vis spectroscopy.

RESULTS AND DISCUSSION

The total phenolic content of the extracts was 2010, 2375, and 2520 mg/L gallic acid equivalent (GAE) for sorghum bran extracted at 25, 50, and 80°C, respectively. Thus, the extraction efficiency increased with increase of extraction temperature. Highly crystalline silver nanoparticles formed within a few minutes of adding the silver nitrate solution to the aqueous sorghum extracts. Intense surface plasmon resonance (SPR) peaks were observed at 390 nm, with colloidal silver nanoparticles synthesized using sorghum extracted at 80 °C had the most intense SPR peak, suggesting a higher number of absorbing particles, attributable to increased extraction efficiency with temperature. The synthesized silver

nanoparticles were spherical with an average diameter of about 10 nm. The nanoparticles aggregated to form well separated nanoclusters inside the extract matrix.

Amorphous iron nanoparticles of about 50 nm diameter formed instantaneously on adding ferric chloride solution to the aqueous sorghum extracts. The particles agglomerated to form irregular clusters inside the extract matrix. The nanoparticles were primarily composed of iron but oxygen was also present in the EDS spectra suggesting formation of amorphous iron oxyhydroxide. BTB (Fig. 1) does not undergo direct oxidation by H_2O_2 but degrades via free-radical pathways. BTB degraded rapidly in the presence of iron nanoparticles and H_2O_2 , indicating that iron nanoparticles acted as catalyst for free radical production from H_2O_2 . The catalysis of H_2O_2 increased with increasing concentrations of iron nanoparticles, leading to increased rate of degradation of BTB.

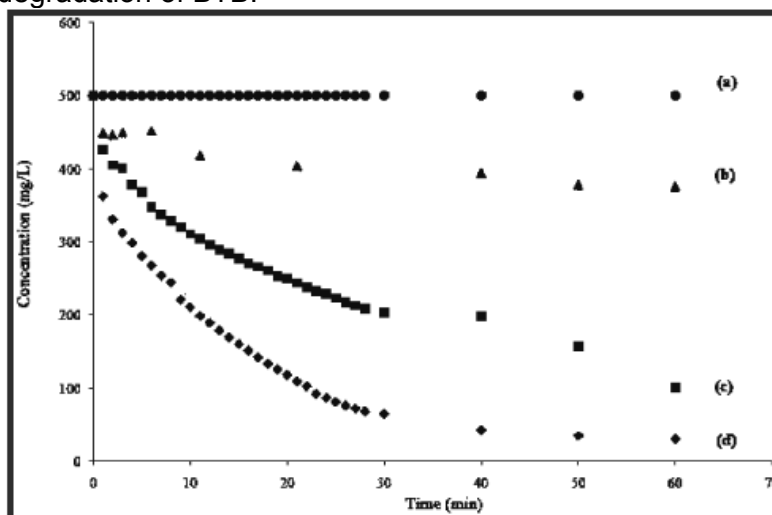


Fig. 1. Degradation of BTB over time with iron nanoparticles catalyzed H_2O_2 : (a) control (BTB with 2% hydrogen peroxide (HP) solution); (b) BTB treated with 0.16 mM (as Fe) iron nanoparticles and 2% HP; (c) BTB treated with 0.33 mM (as Fe) iron nanoparticles and 2% HP; (d) BTB treated with 0.66 mM (as Fe) iron nanoparticles and 2% HP.

CONCLUSIONS

Metallic and metal oxide nanomaterials were successfully synthesized and stabilized at ambient conditions by aqueous sorghum extracts. The synthesized iron nanoparticles effectively catalyzed H_2O_2 degradation of BTB making them potentially useful for environmental remediation and treatment of hazardous waste.

REFERENCES

- Nadagouda, M. N., Hoag, G., Collins, J., Varma, R. S. (2009) Green synthesis of Au nanostructures at room temperature using biodegradable plant surfactants. *Cryst. Growth Des.* 9: 4979-4983.
- Chandran, S. P., Chaudhary, M., Pasricha, R., Ahmad, A., Sastry, M. (2006) Synthesis of gold nanotriangles and silver nanoparticles using *Aloe vera* plant extract. *Biotechnol. Prog.* 22: 577-583.
- Nadagouda, M. N., Castle, A. B., Murdock, R. C., Hussain, S. M., Varma, R. S. (2010) In vitro biocompatibility of nanoscale zerovalent iron particles (NZVI) synthesized using teapolyphenols. *Green Chem.* 12: 114-122.
- Jha, A. K., Prasad, K., Prasad, K. (2009) A green low-cost biosynthesis of Sb_2O_3 nanoparticles. *Biochem. Eng. J.* 43: 303-306.
- Slinkard, K., Singleton, V. L. (1977) Total phenol analysis: Automation and comparison with manual methods. *Am. J. Enol. Vitic.* 28: 49-55.

ORGANOCLAYS FOR ENVIRONMENTAL REMEDIATION

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INTRODUCTION

The Australian continent has huge deposit of clay minerals that are commonly used as clay liners or exported. Naturally occurring clay minerals can suitably be used to reduce the bioavailability of toxic chemicals in water and soil. The underlying principle is adsorption as long as the adsorbed substance is not easily released. The clay minerals are good adsorbents of environmental pollutants due to their inexpensive availability, environmental stability and high adsorptive and ion exchange properties (Sarkar et al., In press) However, naturally occurring clay minerals could be value added by modifying the surface properties. Such modified materials include organoclays prepared by introducing organic molecules into the clay mineral structure. The modified surfaces in organoclays can act as adsorption sink for both organic contaminants and toxic metals and metalloids (Sarkar et al., In press). To this end, this paper describes (a) the preparation of novel organoclays using a range of natural clay minerals and various organic molecules, (b) characterisation of the organoclays using state of the art techniques and (c) elucidation of the atomic scale interaction of organoclays with contaminants in water and soil.

METHODS

Organoclays were prepared by reacting bentonite and palygorskite clay minerals with various quaternary ammonium compounds (QACs) (Table 1) at elevated temperature (Megharaj et al., 2010; Sarkar 2011). The prepared organoclays were characterised by state of the art techniques such as X-ray diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA), particle size and surface area analysis and zeta potential measurement.

The well characterised organoclays were tested for the adsorption of a range of organic and inorganic contaminants in aqueous solutions in batch experiments as well as in flow-through reactor system. The organoclays were also applied to contaminated soils to investigate the adsorbents' ability to reduce contaminant solubility and mobility.

RESULTS AND DISCUSSION

Adsorbent characterisation

Organoclays prepared from bentonite indicated insertion of the surfactant cations into the clay interlayer. The basal spacing of modified bentonite increased up to 35 Å with the increase in surfactant loadings. However, being a non-expanding type of clay mineral, palygorskite did not reveal basal expansion in XRD study. The infrared bands due to symmetric and asymmetric stretching of '-CH₂' group in both bentonite and palygorskite organoclays shifted towards lower frequencies with increasing QAC concentration and conformation of the organic molecules became more regular, ordered and solid-like with an increase in QAC loading. The organic molecules embedded in the clay mineral structure decomposed at temperature between 300 to 450°C and indicated distinctly separate peaks for the elimination of silica surface attached and aggregated surfactant molecules (Sarkar et al., 2010a, b). Modification with the QACs reduced the specific surface area of organoclays by blocking the micropores (Sarkar et al., 2011). The organoclays prepared from bentonite and palygorskite with QACs equivalent to 200% cation exchange capacity (CEC) of the clay minerals contained positive zeta potential (ζ) values as high as 51 and 31 mV, respectively.

The ζ values decreased consistently with increasing pH of the reaction system (Sarkar et al., 2010a, b).

Adsorbent application

The organoclays were proven highly efficient to adsorb range of organic and inorganic contaminants (Table 1). As compared to the natural clay minerals, huge improvement in the adsorption capacities occurred due to the modification. The modified bentonites reduced the bioavailability of arsenic (As) in soil by 81%. Adsorption of metalloids was controlled by complex mechanism of physio-sorption and chemisorptions, whereas partitioning and van der Waals interaction were primary mechanism for organic contaminant adsorption.

Table 1. Adsorption of contaminants by organoclays prepared from bentonite and palygorskite with various surfactant compounds at loading rate equivalent to 200% CEC

Clay mineral	Surfactant	Contaminant	Contaminant adsorption capacity (mg g ⁻¹)
Bentonite	Arquad [®] 2HT-75	Chromium (VI)	14
		Arsenic (V)	4
		Phenol	99
		<i>p</i> -nitrophenol	100
Palygorskite	Hexadecyl trimethyl ammonium	Arsenic (V)	3
	Diocadecyl dimethyl ammonium	<i>p</i> -nitrophenol	42
		Orange II	96
	Octadecyl trimethyl ammonium	Orange II	99
	Cetylpyridinium	<i>p</i> -nitrophenol	36

CONCLUSIONS

The developed organoclay adsorbents can remediate ionisable organic contaminants and heavy metals and metalloids in water and soil. This research delivers new knowledge on some novel adsorbents for the development of an environmental friendly, risk based and cost effective environmental remediation technology.

REFERENCES

- Mallavarapu M., Naidu R., Xi Y., Sarkar B. Modified clay sorbents. CRC CARE Pty Ltd. International Patent Publication Number: WO 2010/065996 A1. Publication date: 17 June 2010.
- Sarkar B. (2011) Remediation of environmental contaminants by novel organoclay adsorbents. PhD Thesis. University of South Australia, Mawson Lakes, Australia.
- Sarkar B., Xi Y., Megharaj M., Krishnamurti G.S.R., Bowman M., Rose H., Naidu R. (In press) Bio-reactive organoclay: A new technology for environmental remediation. *Crit. Rev. Env. Sci. Technol.* (In press).
- Sarkar B., Xi Y., Megharaj M., Krishnamurti G.S.R., Naidu R. (2010) Synthesis and characterisation of novel organopalygorskites for removal of *p*-nitrophenol from aqueous solution: Isothermal studies. *J. Colloid Interface Sci.* 350: 295-304.
- Sarkar B., Xi Y., Megharaj M., Krishnamurti G.S.R., Rajarathnam D., Naidu R. (2010) Remediation of hexavalent chromium through adsorption by bentonite based Arquad[®] 2HT-75 organoclays. *J. Hazard. Mater.* 183: 87-97.
- Sarkar B., Xi Y., Megharaj M., Naidu R. (2011) Orange II adsorption on palygorskites modified with alkyl trimethylammonium and dialkyl dimethylammonium bromide - an isothermal and kinetic study. *Appl. Clay Sci.* 51(3): 370-374.

EMERGING AND GENOMIC APPROACHES IN BIOREMEDIATION

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INTRODUCTION

Widespread use, accidental spillage, inadequate disposal, large-scale manufacturing activities and leaks of organic compounds have resulted in long-term persistent sources of contamination of soil and groundwater. This is a major policy issues because of adverse effects of organic contaminants on human and environmental health. Current technologies for remediation of contaminated sites include solidification/stabilization, soil vapour extraction, incineration, bioremediation, solvent extraction, chemical treatment, etc. Bioremediation offers an environmentally friendly and economically viable option to remove contaminants from the environments (Singh and Walker, 2006). Three main approaches of bioremediation include use of plants, microbes and enzymatic remediation. All three approaches have been used with some success but are limited by various confounding factors. In this presentation, I highlight these limitations and propose two new approaches that have potential to revolutionise the enzymatic and 'designer' plant technologies of bioremediation

1. Microbial and enzymatic approaches: Use of live cells in bioremediation has inherent practical difficulties (e.g. nutritional requirement, availability of fresh inocula, oxygen demand, etc.). As a result the use of purified enzymes is preferred. Theoretically, xenobiotic-degrading enzymes should be a powerful tool in the bioremediation industry. However, in practice their use is limited due to their short self-life, mainly owing to changes in three dimensional structure, activity of environmental proteases and binding and trapping of enzymes to other substrates in the soil such as clay and organic matter. Additionally, continuous requirements for fresh batch enzymes renders this approach expensive and labour intensive because of difficulties in purifying the enzymes from degradation products. Theoretically, enzymes can be re-used for several catalysis cycles and their immobilization provides extended activity and allows their re-use (Kim and Grade 2006; Singh 2010).

Soil, water and other environmental samples present a vast reservoir of microbes and microbial products that could be harnessed to revolutionise the availability of more efficient enzymes for bioremediation. One gram of a pristine soil is estimated to contain up to 10^4 different species, which potentially represent over one million genes encoding putative enzymes. However, until now, most enzymes have been obtained from microbes that have been cultured and exploited in the laboratory. However, cultured microorganisms only account for <1% of the total environmental microbes and, thus, >99% of microbes are currently uncultivable under laboratory conditions and their potential for applications in industries remains untapped (Singh, 2009). We are using an 'improved' approach to isolate novel bioremedial enzymes from the soil uncultivated majority. The enzymes are then immobilised using nanotechnology to extend half-lives, allow for reusability and improved efficiency. I propose a framework of combined approaches of 'improved' metagenomics and nanotechnology for development of an efficient and economically viable enzymatic bioremediation technology.

2. 'Designer' Plant approach: A bioremediation approach is slow and sometimes inadequate when sites are contaminated with mixed pollutants. For example, current bioremediation options for oil industries mainly focus on removal of simple hydrocarbons. However, other waste such as drill cuttings (DCs) contain a mixture of heavy metals, surfactants, emulsifiers and other complex in-/ organic contaminants. This also applies to wastes from a number of mining industries. We are developing a novel remediation

technology termed 'designer' plants, which harnesses combined capability of plants (removal of inorganic pollutant), and soil & endophytic microbes (for removal of organic contaminants). This technology will provide the basis for producing a customised plant system, which contains microbes (fungi and bacteria) on their roots to degrade complex organic contaminant while introduced pollutant-degrading microbes inside the plant system for degradation of other organic pollutants. The plants are then transferred into contaminated sites. This approach not only leads to simultaneous removal of complex and simple organic plus inorganic contaminants (heavy metals) but also improves soils and groundwater quality at faster rates than conventional bioremediation strategies. This technology will provide additional benefits such as (1) generation of plant biomass for an energy source by industry and (2) use of soils for carbon farming by increasing carbon sequestration in soils.

REFERENCES

- Kim, J. & Grate, J. W. Single-enzyme nanoparticles armored by a nanometer-scale organic/inorganic network. *Nano Lett.* 3, 1219–1222 (2003).
- Singh, B.K. (2009). Organophosphorus-degrading bacteria: ecology and industrial applications. *Nature Reviews Microbiology* 7: 156-164
- Singh B.K., and Walker, A. (2006). Microbial degradation of organophosphorus compounds. *FEMS Microbiology Review.* 30, 428-471.
- Singh, B.K. (2010). Exploring microbial diversity for biotechnological products: the way forward. *Trends in Biotechnology*, 28, 111-116

INDUSTRIAL SYMBIOSIS AND THE UK: THE IMPACT OF THE FIRST 5 YEARS OF A NATIONALLY FACILITATED PROGRAMME

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INTRODUCTION

Industrial Symbiosis is a pioneering aspect of resource efficiency which engages traditionally separate industries in a network to foster innovative strategies for more sustainable resource use. In addition to optimizing material flows it also includes efforts to make best use of energy, water, logistics, assets, experts and facilitating the exchange of best practice/knowledge transfer. It enables the development of business opportunities identified for mutually profitable transactions that find new inputs and outputs for processes, seeking to mirror nature in the way that resources are processed and re-utilized without the generation of 'waste'

The National Industrial Symbiosis Programme (NISP), developed by International Synergies Ltd and delivered in 3 UK regions by URS Scott Wilson Ltd, has achieved significant success during its first 5 years of operation as a national programme. This has been reported in its recent publication 'NISP: The Pathway to a Low Carbon Sustainable Economy'. This has not been by accident, but has arisen as a result of deliberate and careful programme design. The programme in the UK comprises a pro-active, yet business led, facilitated network of well over 12,500 businesses. The network of member organisations is co-ordinated to make better use of resources in a collaborative, and often innovative, manner.

METHODS

Initially, the paper will summarise the context in which the programme has been developed and has operated, charting key drivers such as legislation and economic factors. The current situation regarding the waste management and recycling of several key material streams in the UK will be described.

RESULTS AND DISCUSSION

The means by which NISP has achieved its success will be touched upon; the key outcomes of the programme will then be summarised, describing its impact in terms of carefully measured and verified environmental and commercial benefits. The programme's progress will be brought to life through the illustration of several case studies that show tangible improvements in resource efficiency, i.e. re-use, recycling and energy recovery, mainly in the UK, but also internationally.

The paper will highlight some of the challenges faced with delivering such a programme on a national scale, indicating how these have been resolved and also reveal some of the insights gained over the first 5 years of delivery. Finally, following the description of the UK situation, the potential for industrial symbiosis in Australia will be touched upon before drawing the paper to a close with a review of its likely global future.

SOLIDARITY FOR ENVIRONMENTAL HEALTH IN ETHIOPIA: A QUALITATIVE STUDY OF STAKEHOLDERS' VIEWS

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INTRODUCTION

Environmental health achievements have been characteristic for the successful public health response to the major causes of morbidity and mortality (CDC, 1999). Though the link between public health and environment is clear; maintaining healthy ecosystems supporting healthy human populations remains one of the new millennium's critical challenges (Pruss et al., 2002; Borrazzo, 2003). While the basic environmental processes remain unchanged, the real conditions and circumstances in which individuals are exposed undergo increasing change due to the rising human pressure on the quality of environment (McMichael and Powles, 1999). Solutions require political commitment, concerted action and shared responsibility between different government sectors and the civil society. Because of the intricate link of environment and health; collaboration among government departments and the civil society, capacity-building, dissemination of knowledge and good practices, and integrated action for health and the environment are critical. This paper is aimed at exploring the views and opinions of experts on the collaborative effort among stakeholders for environmental health achievement in Ethiopia.

METHODS

An exploratory cross-sectional study design was used. The study subjects were governmental and nongovernmental organizations providing environmental health services in Ethiopia. More specifically, key people in managerial positions such as heads of the school/department, heads of units, and senior government officials were interviewed and staff members of the selected institution or organization were eligible for in-depth interview. All the selected stakeholders participated in this study were grouped into three panels. A total of 28 in-depth interviews were conducted.

RESULTS

This study addressed issues related to existing environmental health intervention approaches, organizational aspect and collaborative state as perceived by the stakeholders. Existing environmental health promotion approaches and organizational arrangement may not conform the actual environmental health condition. From the survey, there were views consistent in the following aspects: Lack of working guideline for intervention and use of tools may be differing to promote environmental health. This is mentioned to be due to the organizations following their own technical approach. Question of ownership for water and sanitation activities were the major issue and area of conflict between environmental health stakeholders.

CONCLUSIONS

There should be a need to reexamine the organizational arrangement that address environmental health problems of the country and also strengthening multi-sectoral

collaboration by harmonizing priority actions before the whole sentiment set-up to a dilemma-turning environmental health into an institutional orphan.

ACKNOWLEDGEMENT

Financial support from Hawassa University is gratefully acknowledged.

REFERENCES

- CDC(1999)Ten great public health achievements--United States, 1900-1999. MMWR. 48:241
- Prüss, A., Kay, D., Fewtrell, L. and Bartram, J.(2002)Estimating the Burden of Disease from Water, Sanitation, and Hygiene at a Global Level. Environ Health Perspect. 110:537–542.
- Borrazzo, J. (2003)Walling R Falk H. Overview of international health. International Journal of Hygiene and Environmental Health. 206: 257-262.
- McMichael, A.J., Powles, J.W.(1999)Human numbers, environment, sustainability and health. BMJ.319: 977–80.

VALUE-BASED LAND REMEDIATION: A CASE STUDY OF EU-FUNDED CONTAMINATED SITE REHABILITATION OF LAMI DUMP, FIJI

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As donor and facilitator of technical assistance, over the last 10 years the European Union (EU) has played an influential role in shaping the approach to cleanup of Lami dump, near Suva in Fiji. This paper presents a CRC CARE-funded case study mapping the decision-making approaches and stakeholder involvement in the site rehabilitation. The premise of this focus is that to achieve the evolving goals of “sustainable” remediation, co-evolution of decision-making approaches, institutions and governance structures is required. The overarching analytical framework underpinning this research is *Institutional Analysis and Development* (IAD). The research was based on interviews with stakeholders representing donors, national and local government, and civil society in Fiji.

ABSTRACT

European countries have long pioneered innovative technical and policy approaches to contaminated site remediation. Over the past 30 years, government policy and legislation facilitating site cleanup have enabled the development of a significant international remediation industry, as well as extensive R&D efforts focusing on cleanup technology, measurement and risk-based assessment techniques. Currently, European as well as North American researchers and practitioners are leading global trends towards “sustainable remediation” (Simon 2009, SuRF-UK 2009). An evolving concept, sustainable remediation frameworks such as the United Kingdom’s Sustainable Remediation Forum (SuRF-UK) and the US Environmental Protection Authority’s green remediation initiatives are characterised by the goal of balancing economic, environmental and social benefits from remediation against the costs (SuRF-UK 2009, US EPA 2008). Fundamentally, sustainable remediation could arguably represent a paradigm shift that extends remediation decision approaches beyond least-cost risk-reduction to embrace the idea that the *problem* of site contamination could be turned into an *opportunity* for value creation and sustainable development: from greenhouse gas emissions to generation of jobs, to enhanced urban liveability.

The reach of the sustainable remediation practice has recently extended beyond Europe and North America; for example, there are emerging developments in Australia to develop a sustainable remediation framework modelled on the SuRF-UK approach. Furthermore, through its role as donor and provider of technical assistance, over the last 10 years the European Union (EU) has played an influential role in shaping the approach to cleanup of a major site, Lami dump, near Suva in Fiji. Although the context differs markedly from developed countries (this is, for example, the first major remediation of its kind in the entire South Pacific), the goal of creating development value from the previously problem site, and how to best go about achieving this, is at the core of the remediation issue.

This paper presents a case study mapping the decision-making approaches and stakeholder involvement in the rehabilitation of Lami Dump. For many decades, pollution from Lami dump has affected the human health, amenity and environmental condition of Suva Harbour, surrounding informal settlements and local through traffic, including visual amenity impacts, foul odour, toxic fumes (from fires), and leaching to coastal environments. In 2005 a major fire at the site that spread fumes and odour across Suva city instituted the EU's decision to fund a new landfill, and after several years of negotiations, in 2010 a contract was signed between the EU and the Fiji Ministry of Finance to rehabilitate Lami Dump.

This Lami dump case study is part of broader research into “values-based” contaminated site remediation policies, and specifically the decision processes undertaken within the site remediation context. The premise of this focus is that to achieve the evolving goals of “sustainable” remediation, co-evolution of decision-making approaches, institutions and governance structures is required. The overarching analytical framework underpinning this research is *Institutional Analysis and Development* (IAD), developed by Nobel Prize winner Elinor Ostrom and colleagues at the University of Indiana, USA. This framework allows the researcher to systematically analyse the structure of situations faced by individuals (‘actors’), and to determine how rules, the nature of events, and the attributes of the local community and surrounding natural environment affect these situations over time (Ostrom, 1994, 2005).

IAD has been extensively applied to investigate common-resource allocation issues; in this research, the “commons” is not a resource like fisheries, forests or water per se, but the land on which the remediation is occurring and the potential array of development values that could be generated from its cleanup. In the Lami dump case study, In the analysis, IAD is used as a guide rather than a recipe; the analysis draws on elements of the IAD framework to analyse the situation at the collective choice level, and in particular drawing on the notion of formal and informal rules to describe the influences on stakeholder actions, including the complex and changing landscape of Fiji’s contemporary land tenure laws and practice. IAD

Recognising that several stakeholders are involved in decisions about remediation and land planning concerning the Lami dump, the research involved investigating the processes for promoting collaboration and coordination between different stakeholders, with an aim is to achieve better remediation decisions and outcomes for the environment and stakeholders, locally, nationally and regionally. The research involved engaging and interviewing stakeholders representing EU donor, EU contractor, local research, municipal and national government, and civil society perspectives. More than twenty semi-structured interviews were conducted to investigate and document learnings from successful and effective collaborative approaches across these sectors.

The paper concludes with a series of findings and reflections on challenges and opportunities of relevance for donor and other stakeholders involved in contaminated site remediation in the Pacific region. This includes issues around communication about public health impacts; building knowledge, capacity and governance structures to enable linking risk, rehabilitation and site redevelopment decisions; promoting collaborations between government departments and universities; collaborations between government agencies; option identification and selection; and contracting and donor administration requirements.

ACKNOWLEDGEMENTS

Funding for this research was provided by CRC CARE.

REFERENCES

- Ostrom E, 1994. *Rules, Games, and Common Pool Resources*. The University of Michigan Press, Ann Arbor.
- Ostrom E. 2005. *Understanding Institutional Diversity*. Princeton University Press, Princeton.
- Simon J 2009. Editor's perspective - Sustainable remediation gains momentum as SURF publishes groundbreaking white paper. *Remediation Journal*. 19, 1-3.
- SuRF-UK (The United Kingdom’s Sustainable Remediation Forum) 2009. A Framework for Assessing the Sustainability of Soil and Groundwater Remediation. Draft Copy Subject to Public Consultation, May 2009.
- US EPA (United States Environmental Protection Authority) 2008. Incorporating Sustainable Practices Into Remediation.

UNDERSTANDING THE POLICY PROCESS: COMPARING LESSONS FROM THE NETHERLANDS AND AUSTRALIAN EXPERIENCE

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INTRODUCTION

Universities, research institutes, such as CRC CARE in Australia and the National Institute for Public Health and the Environment (RIVM) in the Netherlands, and practitioners in the field of contamination assessment and remediation, are continually pushing the knowledge boundary in regards to the assessment and remediation of contaminated sites. Technological development allows more accurate, rapid and cost-effective detection and measurement of contaminants in soil and groundwater; knowledge of the effects of contaminants on human health and the environment is increasing, and methods to more effectively and efficiently (including cost efficiency) remediate contamination are developing continually.

Socio-economic factors, including land use planning processes, are increasingly amongst the drivers for assessment and remediation of contaminated sites, with new approaches such as green remediation and sustainable remediation, developing in the US, the UK and Australia.

Researchers and practitioners expect this 'new knowledge' (science, technology and socio-economic factors) to be picked up immediately by the regulators and often lament the perceived slow pace of incorporating this knowledge into policy and legislation (Schrefler, L. 2010). A number of questions arise from this perception: what drives policy development; how does new knowledge enter the policy-making process and why do some jurisdictions appear to be early adopters and incorporate and implement new knowledge rapidly, and others appear to take so long that the 'new knowledge' has itself been overtaken by more recent research?

DISCUSSION

Incorporation of new knowledge into existing policy and legislation often takes a long time. At the national level in Australia, for example, the review of the National Environment Protection (Assessment of Site Contamination) Measure (NEPM) has been underway for well over six years, while proposed amendments to the principal Act under which NEPMs are made, the *National Environment Protection Council Act 1994*, appears to have stalled. Why is this so?

Using the concept of the 'policy cycle', (Althaus, C., P. Bridgman, et al. 2007) the presentation examines and attempts to address these questions by comparing and contrasting the Netherlands, as an example of an early innovator and adopter, to Australian examples, such as South Australia. Historically, the US is usually seen as the first country to introduce legislation, in 1976, to manage contamination through the *Resource Conservation and Recovery Act* followed in 1980 by the *Comprehensive Environmental Response, Compensation and Liability Act* (CERCLA), better known as the 'Superfund'. In Europe, the Netherlands was the lead nation in developing a policy position and introduced legislation in 1983 to manage contaminated land (the *Interim Soil Cleanup Act*). In contrast, Western Australia did not have a comprehensive legislative base for the management of contaminated sites before the *Contaminated Sites Act* passed through the Parliament in 2003 while South Australia did not amend its *Environment Protection Act 1993* to incorporate site contamination provisions until late in 2007. In both WA and SA, the provisions did not come into operation fully until sometime after proclamation: 2006 and 2009 respectively. Were there specific 'trigger factors' that led the US and the Netherlands to lead the field by introducing contamination management policy and legislation, and were there actual or perceived barriers to explain the slow development of policy and legislation in some

Australian states? Importantly, why does the Netherlands appear to be more responsive to incorporating new knowledge into policy and legislation than Australia?

In addressing these questions, reference will also be made to research currently being undertaken in the Asia Pacific region to address the question: in view of the amount of international scientific (including social science), policy and legislative information available, why have some countries in the Asia Pacific region developed a system for the management of site contamination and others not?

REFERENCES

Althaus, C., P. Bridgman, et al. (2007). *The Australian Policy Handbook*. Crows Nest NSW, Allen & Unwin.

Schrefler, L. (2010). "The Usage of Scientific Knowledge by Independent regulatory Agencies." *Governance: An International Journal of Policy, Administration and Institutions* 23(2): 309-330. _1481 309..330

Hage, M., P. Leroy, et al. (2010). "Stakeholder participation in environmental knowledge production." *Futures* 42: 254-264.

EFFECTIVE RISK COMMUNICATION TO ENABLE A SCHOOL EXPANSION ON A SITE WITH ELEVATED METHANE

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INTRODUCTION

This project demonstrates what can be achieved when good science is combined with effective communication and a pragmatic approach to deliver what initially seemed an impossible task. Through early risk identification and collaboration between key stakeholders with a unified goal, an amazing result was achieved. This project now sets the benchmark for how complex projects with tight timeframes should be delivered.

A school expansion with the construction of 3 new school buildings was proposed before the new school year in February 2011. As part of the local Councils approval conditions, it was determined that the school required an Auditor to complete a Site Contamination Audit Report (SCAR), stating the site was suitable for its intended use and to gain building occupancy approval. To avoid substantial impact to the school, this approval was required within 6 months in order to meet the critical milestone of occupying the buildings before the start of the new school year. The school was built on a reclaimed swamp with the potential for acid sulphate soil (PASS) and was adjacent to a former municipal landfill. Site assessment projects of this complexity, involving an Auditor, typically take much longer than 6 months, with 1-2 years duration not uncommon and even longer if contamination is encountered.

GHD were engaged to undertake an Environmental Site Assessment (ESA) for the site, as part of the audit process. The general objectives of the ESA were to identify potentially contaminating activities, determine the nature and extent of any contamination present on the site, identify the risks that any contamination may pose to environment and human health, and to determine mitigation measures for any identified risks.

ASSESSMENT METHODOLOGY AND OBSTACLES

Phase 1 of the ESA methodology followed industry best practice and involved a desktop review of historical information pertaining to the site, as well as a site inspection and interviews with key stakeholders to determine specific stakeholder needs and concerns.

Phase 2 of the site investigation was developed with consultation with the Auditor, SA EPA and the School representative to ensure that the project outcomes were aligned with expectations of all stakeholders and that the project could be delivered quickly and efficiently but still meet regulatory requirements.

Phase 2 involved intrusive investigation by way of a grid-based soil-sampling program to characterise the site in accordance with the Australian Standard 4482.1 – 2005. Targeted soil sampling was also undertaken during construction of monitoring wells and vapour bores. In addition, samples were collected to assess the suitability of stockpile of imported sand for use as top dressing on the school oval. The results indicated minimal soil contamination across the site and the stockpile was suitable for use as top dressing. Soil samples were also analysed for the presence of Potential Acid Sulphate Soil (PASS) using the SPOCAS method. Based on the results there was no potential for PASS to exist beneath the site.

Three groundwater monitoring wells were installed on site and groundwater monitoring was undertaken to assess the groundwater. The groundwater analytical results were not seen to pose an unacceptable risk to human health and the environment.

A staged approach was implemented for assessing soil vapour which initially comprised the installation of 8 soil vapour bores and undertaking 2 rounds of vapour monitoring. The first round of monitoring identified >20% v/v methane present in a vapour bore. This is above the upper explosive limit of 15% v/v and was identified as a potential showstopper for not only

the school building construction project, but also the future operation of the school. GHD notified the SA EPA and the Auditor and installed additional vapour bores and landfill gas wells and undertook further soil vapour monitoring and assessment. The school liaison was informed as this was an issue that could delay the development and affect the school environment. A week of continuous monitoring in the 2 landfill gas monitoring wells using “gasclams” was undertaken. Air quality measurements were also undertaken using a landfill gas meter within the existing site buildings and below floor cavities in the school where accessible.

RISK COMMUNICATION

A wide range of stakeholders were involved in obtaining building occupancy, including the school representatives, the South Australian Environment Protection Authority (SA EPA), SA EPA accredited Auditor (Anthony Lane of LanePiper), the Local Council, the consulting architect for the new buildings and site construction engineers. Although not within the scope of their investigation, GHD recognised that to achieve project success all stakeholders needed to work together in a collaborative manner, and therefore took control of managing the risk communication for the project. It was vital to build a good relationship quickly with the stakeholders to ensure that the ESA process could be undertaken efficiently and effectively. Barriers to project progress were identified and mitigated quickly, and GHD placed themselves in a position to deliver a result that minimised any impact to school users at the commencement of the school term.

In order to communicate effectively with all of the relevant stakeholders it was necessary to be able to discuss the assessment and approval process with a wide audience, with varying degrees of understanding of the technical aspects of the project. Communicating technical points in simple language, that can be easily understood by all, was critical in order for all stakeholders to remain engaged in the project and feel confident with the investigation process. While potentially frustrating for the school staff, that were focused on their core business of education, through regular dialogue the seriousness of the issue was explained and a professional attitude to their ongoing responsibilities was adopted. By taking a proactive approach and liaising with the SA EPA, local Council and Auditor immediately following the detection of Methane beneath the site, and by further providing them an effective project plan for the assessment, no delays were encountered and the Auditor was able to approve occupancy prior to the start of the school year.

CONCLUSIONS

Early risk identification, project planning and communication with key stakeholders was essential to enable the school to obtain a SCAR and occupancy approval for the proposed buildings at the school. The project was managed through effective, flexible and consultative project management that required open stakeholder communication, and focused on driving all stakeholders to a “best for project” solution.

This approach built a collaborative culture across the stakeholder groups, where all parties were working towards a common goal, which was achieved by the school occupying the new buildings prior to the start of the school year.

This approach demonstrates the value in early risk identification and effective risk communication to achieve exceptional project outcomes.

REFERENCES

Australian Standard, Guide to the investigation and sampling of sites with potentially contaminated soil, 2005.

A REGULATOR'S PERSPECTIVE ON DECISION FRAMEWORKS

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EPA Victoria, like all environmental regulators, faces a range of diverse challenges associated with protecting and improving the environment. Some challenges are historic, such as legacy pollution sites, others involve limiting the environmental impact of current activities, such as regulation of scheduled premises, whereas other challenges are emerging, such as growing populations, urban sprawl land impacts from new technologies. Unfortunately, all these issues can contribute to deteriorating environmental quality.

The principles in the Environmental Protection Act 1970 (EPA70) point EPA towards taking a transparent, accountable approach to balancing the use and enjoyment of the environment. That is balance between social, economic and environmental priorities consistent with the aspirations of an informed and engaged public. At the crux of this is transparent, robust, consistent and fair decision-making. A point well emphasised in our recent Compliance and Enforcement review.

To this end EPA Victoria, in partnership with the University of New South Wales (UNSW), has been researching and developing a decision-making framework. This Sustainable Decision Framework (SDF) integrates elements currently used by EPA Victoria to make environmental determinations. However, it also adds a range of quantitative sustainability assessment tools, such as life cycle assessment and costing, explicitly engages (or should I use addresses) community expectations, and uses a multi-criteria analysis approach to underpins the overall framework.

As an organisational case study the SDF was applied to a previous EPA Victoria's Authority determination of 'Clean Up to the Extent Practicable' (CUTEP). It was found that the SDF could potentially increase the robustness and improve overall environmental outcomes of current CUTEP decision-making. Specifically it helped address: a) the clearer definition of groundwater remediation objectives, outside of the requirement of the State Environmental Protection Policy (SEPP); b) the lack of quantitative sustainability metrics as part of the CUTEP decision; and, c) the explicit acknowledgement of 'values' (i.e. non-scientific judgement) in the assessment process.

OPPORTUNITIES FOR VALUE CREATION: AN INSTITUTIONAL ANALYSIS OF REMEDIATION DECISION-MAKING PROCESSES AT THREE AUSTRALIAN SITES

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INTRODUCTION

This paper reports on the findings of CRC CARE-funded research that explored the institutional arrangements governing remediation decision-making (RDM) processes at three Australian sites. The research was designed to complement an increasing, yet still limited, body of international research that is seeking to understand and enhance the value that may be created by remediating contaminated sites (NICOLE 2008; CRC-CARE 2009; Simon 2009; SuRF-UK 2009). Its key premise is that a socially-robust sustainable development approach to RDM can be taken and that this approach can create comprehensive “triple bottom-line” value from a former liability. Firstly, the research aimed to elicit insights into the way in which value creation operates within current RDM processes within the Australian context. Secondly, it aimed to provide some guidance on future policy and research opportunities that could enhance value creation through RDM for contaminated sites within Australia.

METHOD

We used the Institutional Analysis and Development Framework (IAD) (Ostrom 2005; Smajgl, Leitch, and Lynam 2009) to systematically enquire into the way in which the RDM processes at three Australia sites supports value creation. The three RDM processes explored were selected from a group of 12 RDM processes based on the fact that they were in different Australian States and represented what their stakeholders perceived as leading edge remediation. Within the context of the IAD framework a RDM process for a contaminated site can be conceptualised as *an institutional structure that involve a range of stakeholders interacting together following certain formal and informal rules that have the potential to create value (Ostrom 2005) from a former liability*. The IAD framework permits comparison between and evaluation of the way in which value is created at the three Australian sites (Ostrom 1994).

Application of the IAD framework to explore the creation of value through Australian RDM processes for contaminated sites requires rich information on stakeholders’ roles within these processes, the breath and depth of the process, the physical conditions, existing formal and informal rules and other attributes that may affect the process. This information was collected through an initial desktop literature review, followed by case study research, which involved in-depth interviews and Expert Choice Modelling with key stakeholders in the RMD processes at three contaminated sites. Findings were analysed using NVivo 9 software, enabling a rich picture of the way in which RDM processes that exist within Australia affect value creation through the remediation of contaminated sites. The NVivo 9 analysis also informs policy guidance on how value creation may be enhanced, and ascertains the need and direction for further research into value creation through RDM processes.

RESULTS AND DISCUSSION

It is anticipated that the (as yet unreported) primary research from this project will add significantly to the state of the art in understanding of how value is created through RDM processes associated with contaminated land in the Australian context. Empirical findings will be ready for presentation at CleanUp11 and will encompass insights into how RDM processes and their various attributes - including stakeholder relationships; technological and geographic factors; information flow; formal and informal rules - influence the ways in which value can be created.

CONCLUSIONS

This project is significant given the limited existing international and Australian research on how to maximise value (including actual and perceived risk reduction) through the remediation of contaminated sites. To our knowledge the application of the Institutional Analysis and Development framework, initially designed to address common pool resources, to the issue of site contamination and remediation, has not been undertaken elsewhere. We envisage that findings from our enquiry into the governance dimensions of site cleanup will add significantly to international research currently being undertaken on sustainable and green remediation. When completed, the project is expected to provide a highly useful resource for the broader community of stakeholders involved in RDM processes – neighbours, auditors, regulators, owners, remediation consultants and remediators.

ACKNOWLEDGEMENTS

Funding for this research was provided by CRC CARE.

REFERENCES

- CRC-CARE. 2009. A Framework for Assessing the Sustainability of Soil and Groundwater Remediation Sustainable Remediation Forum (SuRF) Australia; Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE); Australian Land and Groundwater Association (ACLCA)
- NICOLE. 2008. Report of the NICOLE Workshop: Environmental Decision Support Systems. edited by P. Bardos. Madrid.
- Ostrom, E.; Gardner R; Walker, J;. 1994. *Rules, Games, and Common Pool Resources*. Ann Arbor: The University of Michigan Press.
- Ostrom, E. 2005. *Understanding Institutional Diversity*. Princeton: Princeton University Press.
- Simon, J.A. 2009. Editor's perspective - Sustainable remediation gains momentum as SURF publishes groundbreaking white paper. *Remediation Journal* 19 (3):1-3.
- Smajgl, A., A. Leitch, and T. Lynam, eds. 2009. *Outback Institutions: An application of the Institutional Analysis and Development (IAD) framework to four case studies in Australia's outback*. : Desert Knowledge Cooperative Research Centre, Alice Springs.
- SuRF-UK. 2009. A Framework for Assessing the Sustainability of Soil and Groundwater Remediation. Draft Copy Subject to Public Consultation May 2009.: Sustainable Remediation Forum UK.

EMERGING CONTAMINANTS IN THE ENVIRONMENT

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ABSTRACT

Emerging contaminants (ECs) have been widely distributed in the environment and attracted increasing attention over the past decades. In this paper, the contaminants including pharmaceuticals and personal care products, surfactants and their degradation products, plasticizers, pesticides, and fire retardants are comprehensively reviewed. Their main categories, properties, followed by their occurrences and behavior (fate and transport) in natural and engineered systems are discussed. The fate of the nanomaterial in different environmental compartments as well as their effects on human health and other fauna are also presented in this paper. Furthermore, the emerging molecular biology techniques to enumerate microbes capable of degrading ECs are introduced. The study has clearly showed the presence of complex mixtures of emerging contaminants, having various origins, and raised the concern about their potential interactive effects in the environment.

REGULATION OF PFOA UNDER REACH

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INTRODUCTION

Poly- and perfluorinated chemicals (PFC), in particular perfluorooctanesulphonic acid (PFOS) and perfluorooctanoic acid (PFOA), are increasingly detected in the environment and in organisms including humans. Due to their chemical structure, PFCs are very stable and possess unique properties. They are water and grease repellent. Therefore, PFCs are widely used in industry (Kissa, 1994). PFCs, however, are problematic for human beings and for the environment. They are synthetic compounds which are hardly degradable or mineralizable in the environment. Some of them are not degradable at all. Depending on the species, once PFCs are released into the environment, they might persist for a long time. Per- and polyfluorinated compounds have been found ubiquitously in the environment, e.g. in arctic animals, in the deep sea, in rivers (Ahrens, 2011). Especially the persistence in human blood and breast milk after uptake via nutrition, contaminated drinking water or contaminated air is of very high concern (Fromme et al., 2009).

REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the **R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemical substances. One important aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance innovation and competitiveness of the EU chemicals industry. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH. Authorization, harmonized classification and labelling and restriction are risk management options under REACH.

OBJECTIVES FOR RISK MANAGEMENT

The ubiquitous presence of PFCs in the environment is resulting from human activity. There is no known natural source of these substances. Precursors, e.g. perfluoralkylic alcohols or fluorinated polymers can be degraded to perfluoralkylic acids under environmental conditions. These precursors are present in the environment as well, without having a known natural source. Also there are certain measures to reduce use and emissions of PFCs. However, they are still used in industrial and consumer products, i.e. paper packaging, textiles, impregnating agents cosmetics, greases and lubricants, paints, polishes and adhesives (Kissa, 1994). PFOA is primary used to produce its salts, which are used as essential processing aids in the production of fluoropolymers and fluoroelastomers. Releases of PFOA and its precursors into the environment may occur during manufacture and processing operations as well as during the use and disposal of industrial and consumer products containing these substances. PFOA can also be present as residual in polymers and can be released during use of these polymers.

RISK REDUCTION MEASURES UNDER REACH ON THE EXAMPLE OF PFOA: Classification and Labelling

In March 2010 Norway submitted an Annex VI-Dossier to ECHA suggesting to classify and label PFOA as Reprotox. Cat 2. and include the substance in Annex VI of the Regulation for Harmonized Classification and Labelling (CLH). It has been demonstrated, that PFOA is tumorigenic and immunotoxic in rodents and has significant reproductive and developmental toxicological impacts in mice and humans. At the moment the Risk Assessment Committee (RAC) of the European Chemicals Agency (ECHA) is preparing an opinion.

Authorization:

UBA is convinced that PFOA fulfils the PBT-criteria (persistent, bioaccumulative and toxic) of the REACH regulation. Therefore, the identification as substance of very high concern is the first step of risk management concerning the exposition of the environment and humans due to PFOA. Before the Member State Committee decides on the proposal, the dossier will undergo a public consultation period. If the Member State Committee identifies PBT or vPvB properties of PFOA, it will be added to the so called Candidate List. The inclusion of a substance into the Candidate List obliges the manufacturer or importer to inform the ECHA and consumers if products contain more than 0.1 % (w/w) of the substance.

Because of the wide dispersive use of PFOA in numerous consumer products together with low fractions of PFOA in these products (usually less than 0.1% information duties by the manufacturers or importers are not met) further measures are necessary.

Subsequently a substance can be included into Annex XIV of the REACH regulation, which is than subject to Authorization. The inclusion of PFOA into Annex XIV, however, will not help to reach the goal of minimized exposition of humans and the environment, because authorization is not applicable on the import of PFOA containing products. Moreover, PFOA precursors cannot be controlled.

Restriction:

Another measure to reduce risks of substances is restriction. Member states provide Annex XV-dossiers. After a compliance check, the dossier enters a public consultation period and is subsequently reviewed by the Risk Assessment Committee (RAC) and the Committee on Socio-economic Analysis (SEAC) of the ECHA. The harmonized opinion of both committees on the restriction proposal is the basis of decision at the European Commission.

A restriction on marketing and use of PFOA, certain precursors, and products containing PFOA-residues is the appropriate way to limit the risks for human health and the environment. Especially, the import of products containing PFOA can be controlled this way. Before including PFOA and relevant precursors in Annex XVII, the identification as an SVHC seems to be useful due to the information requirements of REACH for consumers and authorities.

REFERENCES

- Kissa E. 1994. Fluorinated surfactants: Synthesis, properties, and applications. Marcel Dekker, New York.
- Ahrens L. 2011 Jan. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J Environ Monit* 13(1):20-31.
- Fromme H, Tittlemier SA, Volkel W, Wilhelm M, Twardella D. 2009. Perfluorinated compounds - Exposure assessment for the general population in western countries. *Int J Hyg Environ Health* 212(3):239-270.

ASSESSMENT OF SEDIMENT TOXICITY IN KAOHSIUNG HARBOR, TAIWAN

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ABSTRACT

In this study, sediment samples were collected from the river outfalls, fishing ports, shipyards, and industrial zone docks of Kaohsiung Harbor, Taiwan to evaluate the distribution of polycyclic aromatic hydrocarbons (PAHs), heavy metals, nutrients, and total organic carbons in sediments. The contamination and toxicity levels of sediments were determined using different sediment quality guidelines. The effect of grain size, enrichment factor, and geo-accumulation index on metal concentration in the sediments were also evaluated.

Results from the sediment analyses show that the sediments contained significant amounts of organics, nutrients, and metals. Based on the analyses using the sediment quality guidelines, Kaohsiung Harbor sediments were moderately contaminated based on the analytical results of total organic carbon (TOC) (ranged from 1.1 to 5.4%), total nitrogen (TN) (ranged from 1,601 to 4,297 µg/g), total phosphorus (TP) (ranged from 282 to 649 µg/g), and heavy metals including Hg (ranged from 0.39 to 2.99 µg/g), Pb (ranged from 11 to 82 µg/g), Cd (ranged from 0.11 to 1.30 µg/g), Cr (ranged from 14 to 473 µg/g), Cu (ranged from 16 to 284 µg/g), and Zn (ranged from 96 to 1071 µg/g).

Results reveal that the industrial activities and urban sewage effluents are the major sources of heavy metal and organic contamination in the harbor sediments. Results from the PAH analyses show that the total PAH concentrations varied from 472 to 16,201 ng/g dry weight, with a mean concentration of 5,764 ng/g dry weight. The highest PAH concentrations came from the industrial zone docks situated in south Kaohsiung Harbor, ranging from 8,788 to 16,201 ng/g dry weight. Among those sediment samples, the 5-, 6-ring PAHs were predominant PAH congeners in sediments, ranging from 42 to 71%. However, the dominant PAH congeners were 2-, 3-ring PAHs (37 to 42%) collected from steel industrial zone docks. This indicates that the sources for the PAH contamination at steel industrial zone docks were different from the other zones in Kaohsiung Harbor.

According to the molecular indices, the possible source of PAHs in the industrial zone dock could be coal combustion while in the other zones it could be petroleum combustion. The total PAH levels were expressed as the total toxic benzo[a]pyrene (BaP) equivalent (TEQ^{carc}). The total TEQ^{carc} varied from 55 to 1,964 ng TEQ/g dry weight. Higher total TEQ^{carc} values were found at industrial zone docks (from 1,404 to 1,964 ng TEQ/g dry weight).

As compared with the US Sediment Quality Guidelines (SQGs), the observed levels of PAHs at industrial zone docks exceeded the effects range low (ERL), and could thus cause acute biological damage. However, the lower levels of PAHs at the other zones would not exert adverse biological effects. Results from this study also demonstrate that the sediment quality guidelines are useful tools for decision-making on managing the dredged materials.

SOURCES, FATES AND EFFECTS OF EMERGING CHEMICALS, WITH EMPHASIS ON THE PEARL RIVER DELTA, ONE OF THE WORLD'S MEGA DELTAS

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INTRODUCTION

The major purpose of this article is to review the historical aspects of environmental pollutants. A large amount of different chemicals has been commercialized for various medical or industrial applications. They were thought to be harmless to the environment and human health, but it has now been gradually found that they are not. The term "Emerging Chemicals of Concern" is therefore a moving target, which is time and location dependent (Wijbenga & Hutzinger, 1984).

THE EARLY DAYS OF ENVIRONMENTAL POLLUTANTS

In terms of water pollution, pathogenic organisms causing various waterborne diseases were of much public concern in the early days (1950's). Water was tested for indicator organisms which accompanied fecal contamination with coliform group the most common bacterial indicator (APHA, 1995). Measuring different nutrients such as nitrogen and phosphorus were important in the 1970's to ensure that these plant growth nutrients would not give rise to algal bloom and red-tides (Middlebrooks et al, 1971); while chlorophyll-a was commonly employed for measuring phytoplankton biomass (Holm-Hansen & Riemann, 1978). The problem of water pollution due to chemical pollutants came slightly later. During 1970's and 1980's testing of heavy metals was regarded as being important to safeguard the water quality (Hutchinson & Meema, 1987).

EMERGING CHEMICALS OF CONCERN

Efforts were made during the 1990's on detecting persistent organic pollutants (POPs), such as DDTs and PCBs, which shared these common properties: (1) very persistent; (2) bioaccumulative and lipophilic; (3) highly toxic to biota; and (4) able to travel long-distance through air and water (Whyllie et al, 2003). From 2000 onwards, accompanied with the advancement of analytical techniques, more and more toxic chemicals have been detected in the environment. A study showed that new born babies contained over 200 chemicals including pesticides, PCBs and plastic additives (such as bisphenol A), in their umbilical cord blood (Goodman, 2009).

SOURCES AND FATES OF EMERGING CHEMICALS

The sources of these chemicals are from residential wastewater, agriculture and consumer products, including pharmaceuticals. Sewage treatment works were designed to treat domestic sewage but not these chemicals. In fact, most of these chemicals could not be removed effectively during different treatment processes, and a substantial amount of these chemicals are concentrated in the sludge. The major concern is that these chemicals have been in the environment for as long as they have been on the market. In particular, they are of relatively recent origin and have not been included in regular monitoring programs, with no limits set for their safe levels of concentration in the environment.

ENVIRONMENTAL AND HEALTH EFFECTS OF EMERGING CHEMICALS

There are various pathways for these emerging chemicals, entering into the food chain and exert adverse effects on different biota, which include changes in the sexuality of different aquatic organisms, e.g. hermaphroditism has been found in African clawed frogs exposed to atrazine (25 ppb) (Hayes et al, 2002). The effects of most of these compounds have not been tested on humans. However, it has been observed that they mimic natural hormones and interfere with human physiology, and affect semen quality (Olea & Fernandez, 2007). In

addition, the health risk of long-term chronic exposure to suites of trace contaminants in drinking water is largely unknown (Benott et al, 2009).

CURRENT SITUATION IN THE PEARL RIVER DELTA (PRD)

Being the most developed region in China, PRD has suffered from severe environmental problems. A recent example is contamination of heavy metals (notably Hg) and emerging chemicals (e.g., DDTs, PBDEs) in freshwater and marine fish cultivated in the region (Cheung et al, 2008). A significant correlation was noted between POPs concentrations (especially DDTs and HCHs) found in human milk and the age of the donors especially those who have a high proportion of locally reared fish in their diet, (Wong et al, 2002). Significant correlations between POPs concentrations in adipose tissues in patients with uterine tumours were also observed, which were linked with their seafood diet (Qin et al, 2010). A subsequent study analysing the blood plasma supplied by the Red Cross indicated that HCH concentration was rather high, when compared with other countries (Qin et al, 2011).

INTERNATIONAL CONVENTIONS FOR CONTROLLING EMERGING CHEMICALS

Currently, there are three conventions: Basel Convention, Rotterdam Convention and Stockholm Convention, which are established to control the abuse and movement of problem chemicals. There is also a problem with the movement of electrical and electronic waste (WEEE) across boundaries, where primitive e-waste recycling methods (typically via open burning) release toxic chemicals into the environment, imposing serious environmental and human health concerns (Wong et al, 2007). The European Union has introduced regulations to control the recycling of electrical and electronic equipment (EEE) waste and to prohibit the use of certain toxic chemicals in manufacturing EEE.

CONCLUSION

Controlling the sources and fates of emerging contaminants is difficult but not entirely hopeless because some confidence can be drawn from previous experience with other chemicals such as DDTs and PCBs. The long-term exposure to low levels of mixtures of emerging chemicals should not be neglected.

REFERENCES

- American Public Health Association (APHA) (1995) Standard Methods for the Examination of Water and Wastewater (19th Ed), APHA, Washington, DC.
- Benott MJ, Trenholm RA, Vanderford BJ, Holady JC, Standord BD, Snyder SA (2009) *Environ Sci Technol* 43: 597-603.
- Cheung KC, Zheng JS, Leung HM, Wong MH (2008) *Chemosphere* 70:1707-20.
- Goodman S (2009) *Sci Am* Dec 2: 5.
- Hayes TB, Collins A, Lee M, Mendoza M, Noriega N, Stuart AA, Vonk A (2002) *Proc Nat Acad Sci* 99:5476-80.
- Holm-Hansen O, Riemann B (1978) *Oikos* 30: 438-47.
- Hutchinson TC, Meema KM (1987) *Lead, Mercury, Cadmium and Arsenic in the Environment*. John Wiley & Sons, New York.
- Middlebrooks EJ, Pearson EA, Tunzi M, Adinarayana A, McGauhey PH, Rohlich GA (1971) *J Water Pollut Cont Fed* 43: 242-51
- Olea N, Fernandez F (2007) *Occup Environ Med* 64: 430-1.
- Qin YY, Leung CKM, Leung AOW, Wu SC, Zheng JS, Wong MH(2010)*Environ SciPollut R* 17:229-40.
- Qin YY, Leung CKC, Lin CK, Leung AOW, Wang HS, Giesy JP, Wong MH (2011) *Environ Sci Technol* 45: 1630-7
- Whyllie P, Albaiges, Barra R, Bouwman H, Dyke D, Wania, F, MH Wong (2003) *Regionally Based Assessment of Persistent Toxic Substances*. Global Report. UNEP/GEF.
- Wijbenga A, Hutzinger O (1984) *Naturwissenschaften*. 71: 239-46.
- Wong CKC, Leung KM, Poon BHT, Lan CY, Wong MH(2002) *Arch Environ ContamToxicol* 43:364-72.
- Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AOW, Wong CSC, Lukesmburg WJ, Wong AS (2007) *Environ Pollut* 149:131-40.

NANOMATERIALS AND POLICY – THE INFLUENCE OF RISK ON THE DEVELOPMENT OF POLICY IN AREAS OF EMERGING RISKS

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INTRODUCTION

The link between policy development, regulation and risks is ill-defined. There is a perceived reliance on economic drivers to influence government intervention and to ensure a positive market outcome, however there has also been a movement towards risk-based approach to policy development and regulation within UK Government. In areas where there is a limited evidence base for risk assessments, such as nanomaterials, there is a great deal of uncertainty within the assessment, management and the supporting regulation. Engineered nanomaterials (materials that have one or more external dimensions in the nanoscale; BIS 2007) and their use within research and commercial processes are a topic of great debate; their novelty, morphological variety, potential exposure routes and unknown hazards prove a challenge for any assessor or regulator. Indeed, due to the multidisciplinary, international and exploratory nature of nanomaterials and their related sciences, there are a range of divergent terminology definitions and disciplines which complicate any assessment.

Internationally, there are an estimated 1000 consumer products on the market containing engineered nanomaterials (Project on Emerging Nanotechnologies 2009), including construction materials, clothing, cosmetics and food. The nanomaterials commonly used in consumer products included engineered nanomaterials that have been classified as harmful (Kahru *et al.*, 2010), and therefore suggest that they need regulation to protect receptors (humans, animals and the environment) from potential harm. The current regulation and policy within the European Union and United Kingdom (Directive EC 1907/2006) does not specifically separate nanoscale forms of materials from their bulk forms, which does not take into account their unique morphology, reactivity and translocation potential (Rocks *et al.*, 2009). The Registration, Evaluation, Authorisation & Restriction of Chemicals (REACH) Directive relies on specific weight triggers to prompt for initial assessment and for the level of detail that is required within that assessment. In addition, the assessment methods are not designed to be used with nanoscale particles, making it necessary to adapt standard testing procedures.

METHODS

Structured search of peer reviewed and grey literature were used to identify robust and reliable studies of the risk of engineered nanomaterials, incorporating both hazard and exposure studies. These were then used to develop a conceptual model of the potential environmental release of nanomaterials, which concentrated on the release of the materials into the water system and the subsequent treatment and potential end locations. In addition, a survey of identified experts from the UK and US was used to value the pathways within the conceptual model. The uncertainty was also measured and collated. The peer-reviewed and published literature, supplemented by expert elicitation, was used to evaluate current risk assessment protocols against the requirements previously identified by SCHENIR (2007).

RESULTS AND DISCUSSION

Risk assessment methodologies (n=6) were identified as potentially applying to engineered nanomaterials. There was not a method identified that fully addressed the known knowledge gaps (stated in previous publications; SCENHIR 2007; Rocks *et al.*, 2009). Essential information for the risk assessment was considered to include morphology, surface area, agglomeration/aggregation potential, particle number and persistence.

The identified essential information, in addition to current belief on hazard identification and exposure measurement identified from peer reviewed and grey literature, were used to inform a conceptual model. The model was then evaluated by experts (n = 20) to determine its relevance and accuracy. The altered model was then used by experts as a prompt for the allocation of individual and aggregated values of uncertainty and belief (as determined by expert input).

CONCLUSIONS

This work combines a series of expert elicitation sessions, primary research, and targeted literature reviews on the toxicity and exposure of nanomaterials, along with the potential regulatory mechanisms to present the evidence base and arguments for potential changes to policy and regulation covering the manufacture and importation of nanomaterials. The increased use of nanomaterials and the resultant augmented research have meant that the knowledge base has grown, however it is still a matter of opinion as to whether there is sufficient evidence to influence policy.

We gratefully acknowledge support from EPSRC/ESRC/NERC/Defra (EP/G022682/1), Defra (CB403, CB409), and NERC/US EPA (NE/H01375X/1)

REFERENCES

- BSI (2007) Terminology for Nanomaterials PAS 136:2007 British Standards Institution, London.
- Rocks S.A., Owen R., Pollard S.J., Dorey R.A., Harrison P.T.C., Levy L.S., Handy R.D., Garrod J.F. (2009) Risk assessment of manufactured nanomaterials from Lead J., Smith E. (Eds) Environmental and Human Health Effects of Nanoparticles, Blackwell Science.
- Kahru A, Dubourguier H (2010) From Ecotoxicology to Nanoecotoxicology. *Toxicology* 269:105-119.
- Scientific Committee on Emerging and Newly-Identified Health Risks (SCENHIR) (2007) Opinion on the appropriateness of the risk assessment methodology in accordance with the technical guidance documents for new and existing substances for assessing the risks of nanomaterials, European Commission
- Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Corrigendum version, 29 May 2007).
- Aitken R.J., Hankin S.M., Tran C.L., Ross B., Stone V., Fernandes T.F., Donaldson K., Duffin R., Chaudhry Q., Wilkins T.A., Wilkins S.A., Levy L.S., Rocks S.A., Maynard A.. (2009) EMERGNANO: A review of completed and near completed environment, health and safety research on nanomaterials and nanotechnology CB409 report for Department of Environment, Food and Rural Affairs.

BENCHMARKING OF SUSTAINABLE REMEDIATION DECISION-SUPPORT TOOLS USED IN A TIERED SUSTAINABILITY APPRAISAL FRAMEWORK

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INTRODUCTION

Sustainable remediation comprises soil and groundwater risk-management actions that are selected, designed and operated to optimise the net-environmental, social and economic benefit. Sustainable remediation is designed to contribute to sustainable development, as defined by the Brundtland Commission, and to ensure that the net-benefits of undertaking remediation activities are greater than the impacts (to the environment, society and economy) of undertaking the works.

A variety of sustainable remediation assessment methods are available for assessing the relative merits of different remediation strategies and technologies, such as qualitative screening methods, multi-criteria analysis (MCA), through to fully monetized Cost-Benefit Analysis (CBA). These methods can be applied in a tiered assessment framework, such as that presented by the Sustainable Remediation Forum-UK (SuRF-UK, 2010). Each sustainability appraisal method has a different level of analysis complexity, data requirement, and associated resource and operator-skill to perform, whilst aiming to aid an assessor's decision on remediation selection.

A benchmarking exercise was undertaken on a range of sustainable remediation assessment tools, applied to the risk-management of a petroleum release at a retail filling station site. Three sustainable remediation assessment techniques were included in the benchmarking exercise: Simple qualitative, Multi-Criteria Analysis and fully monetized Cost-Benefit Analysis. The objective of the benchmarking exercise was to determine:

1. whether they would lead to the same environmental management (remedy selection);
2. the costs and time of undertaking a sustainability assessment by each method;
3. the assessor skill requirements;
4. the data requirements.

An ideal sustainable remediation decision-support tool is quick and easy to use, requires minimal capital or human resources, and supports robust management decisions – ideally the same management decisions as would be generated using a much more complex and precise analysis of the options. This paper will describe the tiered assessment framework for sustainable remediation presented by SuRF-UK and the results of the benchmarking exercise for sustainable remediation decision support tools. It will describe how, at least for relatively simple remediation projects, a simple qualitative appraisal produced the same management decisions as more complex appraisal tools.

REFERENCES

SuRF-UK, 2010. *A framework for assessing the sustainability of soil and groundwater remediation*. CL:AIRE, London.

DO OUR CLEAN UP PROJECTS CURRENTLY ACCORD WITH THE CONCEPT OF SUSTAINABLE REMEDIATION?

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INTRODUCTION

“Sustainable remediation” is a topic of intense debate in Australia. The initiatives in the USA and UK involving the formation of a Sustainable Remediation Forum (SURF) are being closely watched, and a similar body has been formed - SURF Australia. Australian regulatory agencies, industry and the consulting companies are supporting the consideration and application of the principles of sustainability in land and groundwater remediation projects.

SuRF Australia has prepared a draft Framework for Sustainable Remediation and Management of contaminated sites. This is consistent with a similar Framework prepared by SuRF UK. A core objective of sustainable remediation is to seek to achieve a balance between the various environmental, economic and social aspects of the project, and a set of indicators to measure this has been proposed in the draft Framework.

It was suggested at a meeting of SuRF Australia in Sydney in March 2011 that our Australian regulatory system already allows for project outcomes that are in good accord with the Framework. Whether this is the case is examined in this paper.

METHODS

Major projects in Victoria, South Australia, the Northern Territory and New South Wales that have been either completed or are well advanced have been assessed against the sustainability indicators, and compared with the probable assessment outcome if other remedial options had been adopted.

RESULTS

The analysis indicates that the Australian regulatory system does allow for outcomes that are in accord with the concepts of sustainable remediation. In particular, it was found, in each case the adopted solution:

- Meets the requirements of the relevant environmental regulatory authority for protection of the environment, and low energy solutions have been adopted that minimise the emissions of green house gases and resource consumption. Options that might have been adopted would also have met the requirements for protection of the environment, but would probably have resulted in greater emissions of green house gases and resource consumption.
- Has sought to minimise the overall cost of the project and to provide maximum economic benefit, and options that might have been adopted would probably have resulted in greater overall cost.
- Has sought to minimise concerns that various stakeholders might have through a consultation process, and in particular to minimise community impact and to maximise community benefit although this has not been formally accounted for. It

seems unlikely that options that might have been adopted would have resulted in a more socially acceptable outcome.

Importantly, each project has a level of risk that is acceptable to the various stakeholders.

It is concluded that the current approach in Australia can provide for solutions to soil and groundwater contamination problems that provide a balance of environmental, economic and social factors, although this is not formally demonstrated through assessing options against a set of environmental, economic and social indicators.

It happens that for each of these projects a low energy approach has been adopted that allows for some contamination to remain in situ with varying degrees of long term management control. Had a high energy complete clean up been mandated then a different balance would have been achieved. It becomes apparent from the assessment that the most important factor in determining the solution that should be adopted is the endpoint that is deemed to be protective of the environment and acceptable to the various stakeholders.

Critical in the analysis is the acceptability, risk and weighting given to:

- Allowing residual contamination, the acceptability of providing for its long term management, and the acceptability of the risk that this results in; and
- Allowing limitation on the use of land or groundwater, the duration over which this limitation is permissible, and whether “practicability” is a factor that is able to be considered.

These are factors that in most cases will require consultation with the regulatory agency and the various stakeholders to determine what is acceptable, and what is unacceptable. This emphasises the importance of stakeholder consultation in the sustainable remediation framework.

A NET BENEFIT APPROACH TO DETERMINING ENDPOINTS FOR ACTIVE REMEDIATION SYSTEMS

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OBJECTIVE

The objective of this paper is to demonstrate that at a certain point in the life of an active remediation system, the net benefit to humanity and the environment of continued operation is likely to become negative. This is despite residual contamination including LNAPL remaining within the subsurface.

INTRODUCTION

At contaminated sites, where it can be demonstrated that risks to human health and the environment are low and acceptable, achievement of milestones to allow site closure or divestment often rely on demonstrating that active remediation has reached an endpoint. Typically, regulation requires restoration of groundwater beneficial uses with removal of LNAPL, where present, as a specific objective. In complex geologies, particularly fractured rock, complete removal of LNAPL and restoration of beneficial uses is rarely possible within reasonable timeframes and a clean-up to the extent practicable approach may be supported.

Defining extent practicable, for LNAPL removal in particular, is rarely simple or consistent and requires multiple lines of evidence to gain support from regulators. Whilst proof is necessarily focussed on recovery type metrics and LNAPL occurrence in monitoring wells, these rely on agreeing an acceptable numerical value beyond which no further active effort is required. As an alternative to recovery type metrics, it is considered that setting remediation endpoints within a net benefit framework is a legitimate part of extent practicable demonstration. In this case, in addition to demonstrating active remediation is at the point of diminishing returns, it may be shown that further remediation is likely to result in a net negative benefit to the environment and society.

The incorporation of net benefit concepts in the development of active remediation endpoints has recently been undertaken on a groundwater remediation project in Victoria, Australia. The general approach is believed to be applicable to a wide range of contaminated land scenarios.

This paper builds on previously presented information and offers discussion on how cessation of active remediation using endpoints that incorporate net benefit may be integrated into decision frameworks.

METHODS

Ongoing and extensive monitoring of remediation system operation at the project site has produced a robust data set that was used to assess the net benefit of continued operation of the active remediation systems. Parameters such as carbon dioxide emissions from power generation, combustion of hydrocarbons and vehicle emissions; electrical power usage; total distance travelled by vehicles involved in operation and maintenance; and financial cost are tracked. Formal analysis is completed using freely available Sustainable Remediation Tools including *SRT - Sustainable Remediation Tool* (US Air Force 2010) and *Site Wise* (US Navy 2010). Qualitative assessment of net benefit is undertaken by placing the expenditures and

outputs in context of activities and ventures that are generally considered to be of positive benefit to humanity.

RESULTS AND DISCUSSION

Through semi-quantitative and qualitative analysis of data collected over a number of years, the net benefit of continued operation of the active remediation was assessed. Approximate numbers for a range of parameters including carbon dioxide production were calculated and an attempt made to provide a wider context. For example, it was calculated that over 2 tonnes per day of carbon dioxide were emitted during active system operation. This is equivalent to approximately 100 cars per day and would require the planting of more than 700 acres of trees to offset.

The assessment was of sufficient validity to gain in-principle support from regulators to shut-off the active remediation systems with condition that contingency plans be developed should ongoing groundwater monitoring show reverse trends and ongoing reduction of mass be demonstrated by passive means.

CONCLUSIONS

At a certain point in the life of an active remediation system, the net benefit of continued operation to humanity and the environment is likely to become negative. This is despite residual contamination including LNAPL remaining within the subsurface.

It is considered that an approach to determination of endpoints of the cessation of active remediation systems will be improved by the incorporation of net benefit aspects.

REFERENCES

- Freeze, R.A. (2000) *The Environmental Pendulum: A Quest for the Truth about Toxic Chemicals, Human Health and Environmental Protection*. University of California Press.
- Havranek, T.J et al (2010) *Sustainable Remediation Panel – Measuring the Social and Economic Benefits of a Sustainable Remediation Project*. Remediation (Winter 2010) pp153-158
- SURF, CRC CARE, ALGA (2009) *A Framework for Assessing Sustainability of Soil and Groundwater Remediation*

PROSPECTS FOR THE UTILISATION OF IN-SITU THERMAL REMEDIATION TECHNIQUES IN AUSTRALIA

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INTRODUCTION

In-situ thermal remediation (ISTR) is a commonly used site contamination remediation methodology in North America and Europe with in excess of 200 projects being completed to date. However, the various ISTR technologies have yet to become widely accepted for use by consultants and stakeholders in Australia. Similarities in site conditions and contamination remediation risk drivers between remediation sites in Australia and documented case studies of highly successful ISTR implementation from North America and Europe are often very apparent. There appears to be no obvious reason for the current lack of uptake of these technologies in Australia apart from reluctance from stakeholders to adopt a method that is not locally well known and a perception from consultants, and other parties involved in remediation procurement, that ISTR technologies are not sustainable. From the author's personal experience in the implementation of ISTR in Europe and knowledge of numerous successful case studies, it is suggested that it is now appropriate to commence utilisation of these mature technologies at appropriate remediation sites in Australia.

BACKGROUND TO ISTR TECHNOLOGIES

ISTR technologies all involve the addition of heat into the ground to enhance the removal of volatile and semi-volatile organic contaminants. As heat is transmitted into soils, various processes occur which lead to mobilisation and degradation of contaminants. These include increases in vapour pressure and solubility, a decrease in the viscosity of separate phase liquids and increases in both abiotic and biological degradation rates. Heat can be introduced to the subsurface by several means, the most commonly utilised of which are the injection of steam, electrical resistance heating, radio frequency heating and thermal conduction heating. These systems are all used in conjunction with a vapour extraction and off-gas treatment system to ensure removal, capture and treatment of mobilised contaminants.

The different technologies all have their strengths and limitations depending on soil and groundwater conditions, the nature of the contaminants, clean-up time frames and site constraints. In some circumstances, such as sites with heterogeneous soils, different technologies are sometimes used in combination to achieve remediation goals.

REMEDICATION TO THE EXTENT PRACTICABLE

The principle of remediation to the extent practicable is widely accepted by Australian regulators whether as, for example, the "Clean up to the Extent Practicable" (CUTEP) approach in Victoria or the elimination of actual or potential harm "as far as reasonably practicable" approach in South Australia.

CUTEP determinations are made on the basis of technical, logistical and financial considerations. ISTR technologies are technically very versatile and can be effectively utilised in a range of soil types and fractured rock in both the vadose and saturated zones (Heron et al., 2008). They have proven to be effective at remediating a wide variety of organic contaminants from solvents and petroleum hydrocarbons through to relatively recalcitrant substances such as coal tar, polychlorinated biphenyls (PCBs) and dioxins in relatively short time frames. Many common logistical constraints can be overcome such that ISTR can be completed beneath existing buildings and even operational businesses (McGee et al., 2002). Typical ISTR treatment costs lie in the range \$100 to \$150 per m³, which

compare favourably with excavation and disposal to landfill as well as many other in-situ and ex-situ remediation options. Higher ISTR costs generally apply when high temperatures and longer treatment times are appropriate for example for in-situ thermal desorption of coal tars or PCBs. When comparing cost of various remedial options it is important to consider total resource costs over time (Baker, 2008); these tend to be limited with ISTR due to the relatively short duration of the projects. With commonly achievable contaminant source mass reductions of >95%, the adoption of ISTR technologies in Australia would enable the “extent” to which “practicable remediation” of organic contaminants can be achieved to be increased significantly compared to some other methodologies currently used.

SUSTAINABLE REMEDIATION CONSIDERATIONS

The Sustainable Remediation Forum (SuRF) Australia has produced a draft framework for assessing the sustainability of soil and groundwater remediation. The framework suggests that sustainable remediation and management can be defined as “*the practice of demonstrating, in terms of environmental, economic and social indicators, that an acceptable balance exists between the effects of undertaking remediation activities and the benefits that those activities deliver*”. The energy input required for ISTR will result in CO₂ emissions during generation, however due to short operation times energy consumption can be relatively low in comparison with other technologies. For example research conducted at four sites by the VEGAS facility in Germany revealed 27% to 59% savings in energy consumption could be achieved using ISTR rather than conventional “cold” soil vapour extraction (Hiester and Schrenk, 2005). Economically ISTR compares well with other technologies (Faurbye et al., 2009) and it has a low environmental impact, generally with minimal community disturbance.

CONCLUSIONS

ISTR offers a sustainable remediation option for many contaminated sites within Australia, notably when one or more of the following circumstances are present:

- Stringent clean-up levels must be achieved
- Rapid clean-up is required
- Relatively high concentrations of contaminants exist
- Excavation is expensive or impractical
- The treatment zone is deep
- There is a mixture of contaminants
- The site is complex and contains existing buildings and/or infrastructure
- LNAPL and/or DNAPL are present within the soil/rock and groundwater regimes

REFERENCES

- Baker, R.S., Bierschenk, J.M., LaChance, J., Galligan, J.P., Tarmasiewicz, D., Heron, G., Leach, W.R. (2008) Why in situ thermal desorption can be the most cost-effective remediation method for many sites *Remediation of Chlorinated and Recalcitrant Compounds: Proceedings of Sixth International Conference*.
- Faurbye, M., Jensen, M., Rugge, K., Nielsen, S.G., Heron, G., Baker, R.S., Johansen, P., Tolstrup Karlby L. (2009) Thermal in-situ remediation – a sustainable choice *Green Remediation Conference, Copenhagen*.
- Heron, G., Baker, R.S., LaChance, J., Bierschenk, J.M., Ploug, N., N., Faurbye, M., Langford, S., Tully, D. (2008) Thermal conduction heating for DNAPL removal in low-permeability soils and bedrock *ConSoil 2008, Milan, Italy*.
- Hiester, U., Schenk, V. (2005) In-situ thermal remediation: ecological and economic advantages of the TUBA and THERIS methods *ConSoil 2005, Bordeaux, France*.
- McGee, B.C.W., Nevokshonoff, B., Keenan, K., and Warren, R.J. (2002) ET-DSP™ for in-situ remediation under an occupied residential apartment building. *ESAA - Remediation Technologies Symposium*.

SUSTAINABILITY METRICS FOR A RANGE OF THERMAL REMEDIATION METHODS

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INTRODUCTION

This presentation discusses selected sustainability metrics for a range of thermal remediation methods, including some that are currently applied in Australian and others that have been applied only in North America and Europe. The metrics have been developed for a remediation scenario based on a high value, capital city property contaminated by hazardous compounds.

OBJECTIVES

The objectives of this paper are to:

- Measure a number of easily measured parameters including time, cost and carbon footprint for a remediation scenario and four different thermal remediation methods;
- Discuss their implications in terms of remediation sustainability; and
- Consider the implications for sustainability of a number of difficult to measure parameters.

METHODOLOGY

The remediation scenario is a hypothetical 5 Ha capital city site, contaminated by high concentrations (20,000 mg/kg) of “hazardous” organic compounds in soil, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) or polycyclic aromatic hydrocarbons (PAHs). The site has been rezoned for medium to high density residential and commercial land use and has to be remediated. For simplicity the scenarios all assume 100,000 m³ of contaminated soil 2 metres thick, either at surface or at depth. The clean up standard is for “unrestricted” land use, that is to a conservatively low standard. The remediation options considered are:

- Excavation and treatment onsite in a continuous rotary Directly-heated Thermal Desorption (DTD) plant, with reuse on site of the treated soil;
- Excavation and onsite treatment in a batch Enhanced Thermal Conduction (ETC) plant, with reuse on site of the treated soil;
- Insitu thermal treatment using the Electro-Thermal Dynamic Stripping Process (ET-DSP), based on insitu electrical resistive heating; and
- Insitu thermal desorption (ISTD), using the insitu electrical conductive process.

The above options all assume use of destructive type emission control systems that use thermal oxidisers to destroy contaminants. Not considered are thermal remediation options that use recovery type emission control systems such as indirectly-heated thermal desorbers (ITDs), used to recover hydrocarbon from sludge and combination systems such as ET-DSP with steam injection.

Typical plant, equipment, labour and utility rates are used to calculate a number of easily measured remediation metrics (assuming current prices) including duration, labour, direct costs, direct and some indirect energy use, carbon footprint (as CO₂equivalent (or CO₂e)) and selected avoided future costs, resources and energy use. CO₂e is a measure of total greenhouse gas impact including contributions from nitrous oxides and methane, expressed as CO₂ equivalents impacts. For the remediation technologies above >99% of greenhouse

gas impacts are from CO₂ produced by combustion of gas and black or hard coal used in electricity generation.

To select the most appropriate thermal remediation method a wide range of other technical matters also have to be considered, some of which may be critical. These include depth and accessibility, whether the target layer is above or below the water table, the nature of the groundwater regime, whether rock is involved, starting concentrations, treatment standards, boiling point of the contaminants, and moisture content, density, resistivity and organic content of the matrices.

RESULTS

When comparing the nominated remediation methods, it is apparent that direct costs for most methods are principally determined by energy use. While excavation, handling and transportation costs are similar for the ex-situ methods, they are dwarfed by energy costs.

However, there are significant differences between energy costs for the various thermal methods. The two ex-situ methods (DTD and ETC) heat the soil either directly (by convection) or indirectly (by conduction) using combustion gas to between 300 and 500 °C depending on the boiling point of the contaminants present and treatment standards. The two in-situ methods heat the soil to either 100 °C (ET-DSP™) or up to 500 °C (insitu conductive), resulting on large differences in energy use. ET-DSP™ combined with steam injection can achieve treatment temperatures of greater than 100°C.

Considering carbon footprint the differences between emissions from gas and emissions from electricity are smaller. This is because the CO_{2e} factor for electricity produced from black coal includes a multiplier that accounts for transmission and other losses.

In practice the choice of which thermal remediation method to use (assuming that a non-thermal method is not applicable) may be determined using other critical considerations. For instance an ex-situ insitu thermal solution would not be possible in a built up area without extensive demolition. In this situation an insitu method would be technically feasible and may be more cost effective considering the cost of demolition, displacement and reconstruction.

Considering only insitu methods, if removal of volatile and soluble compounds is the critical consideration and partial removal of high boiling point compounds is acceptable from a risk, regulatory and community perspective, then the ET-DSP™ and low temperature ISTD conductive method may be equally cost effective.

CONCLUSIONS

The small number of metrics highlighted in this presentation start to illustrate the complexity of remediation decision-making even for a single approach such as thermal remediation, which covers a range of methods.

There are many more metrics, which could be used to inform remediation decision-making, some of which are technical, whilst others are more subjective and value based. Different decision-making parties (eg site owner, remediation provider, regulator, and community) have different values and therefore different priorities and different metrics of importance, and the weighting they are given.

Furthermore remediation decision-making will be determined by both the metrics adopted for analysis and also site-specific factors such as location, zoning, land value, local regulations, the nature and concentrations of contaminants, geological setting, community values and time available. Determination of the most sustainable remediation method for a project will always be site and time specific, and involve consideration of a range of factors some of which are easy to measure and some, which are not.

SUSTAINABLE REMEDIATION EXAMPLES OF GROUNDWATER CONTAMINATED WITH TCE IN A FRACTURED ROCK AQUIFER

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INTRODUCTION

This paper will look at the aspects of applying a low technology groundwater remediation solution to a site adjacent to other sites where no active remediation was conducted. An environmental audit was required for the redevelopment of a former metal forging site proposed for redevelopment for medium to high density inner suburban residential use. At this former metal forging site, oils and degreasers (such as trichloroethylene (TCE)) were used in bulk quantities for the degreasing of metals, for the quenching of metals and for lubricating of machinery.

RESULTS AND DISCUSSION

The properties adjacent to the site had undergone an environmental audit with the audits being completed in 2006. The adjacent sites were essentially vacant, with ongoing monitoring of groundwater quality being undertaken subsequent to the completion of the environmental audit for these sites. The environmental audit included a health risk assessment of the risks posed by TCE in groundwater as well as a Clean Up to the Extent Practicable (CUTEP) assessment and submission (and agreement) with EPA.

Assessment works at the subject audit site were conducted by the environmental consultant and involved the assessment of the shallow soil profile and completion of groundwater investigation works, including the lateral and vertical delineation of the TCE impacted groundwater.

TCE on the subject site was identified at concentrations up to 4,000ug/L, an order of magnitude higher than adjacent sites. The investigation also identified an LNAPL plume in a separate portion of the site.

With the identified pollution of groundwater, some form of active remediation was required. Convincing the landowner of the need for active remediation was difficult in light of the adjacent sites, where no direct active remediation of groundwater was undertaken. With the emphasis of the CUTEP process on "clean up", a method of remediation was developed allowing for the application of EHC-A compound as manufactured and supplied by Adventus for remediation of the dissolved phase TCE.

EHC-A was determined as the most appropriate as:

- The TCE plume was not extensive, with the source zones as well as could be understood and there being monitoring results for groundwater over a larger area for at least 5 years;
- EHC-A creates a reductive zone in the groundwater environment and does not need to come into direct contact with the TCE to create conditions conducive to reductive dechlorination, a key aspect when considering the fractured nature of the basalt aquifer;
- Adventus, as the manufacturers of EHC-A, were able to provide case studies of previous successful applications of EHC-A in regard to TCE remediation; and,
- EHC-A provided a relatively simple and low cost approach to remediation of the TCE that was acceptable from the clients perspective.

- The EHC-A was introduced to the subsurface via 4 open holes drilled into the rock to approximately 2 metres above the saturated portion of the aquifer. The theory behind the application was to introduce the EHC-A at a point close to the key area of residual TCE, but to allow sufficient distance for the EHC-A slurry to imitate the migration pathways of the TCE contaminant within the unsaturated and saturated zones.

CONCLUSIONS

Monitoring of TCE concentrations was conducted 2, 4 and 8 weeks post application of the EHC. The key parameters comprised TCE, DCE, VC, redox, ferrous iron, ethylene and DO. Ongoing monitoring was conducted to measure the potential for contaminant rebound and to measure effectiveness of the EHC-A delivery downgradient of the injection points. Monitoring indicates TCE concentrations initially reduced by an order of magnitude. Upon application of a second larger dose TCE concentrations have reduced a further order of magnitude. As expected, subsequent monitoring has indicated rebound in TCE concentrations, but remaining at least an order of magnitude below conditions prior to remediation. Ongoing monitoring of groundwater quality is expected to occur for an additional 6 months.

Observations made during the remediation include:

- Longer term monitoring indicates that the TCE remediation has been successful.
- Remediation and monitoring costs of less than \$60,000 for the 90% plus reduction in TCE concentrations.
- The approach utilized incorporates all the elements of a sustainable approach to remediation of dissolved phase contaminants within the saturated zone without the need to extensive energy exhaustive remediation approaches.
- The approach has been shown to be a highly effective and successful low cost and low technological approach to remediation of dissolved phase TCE in a fractured rock environment.

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REDUCING SAMPLE VOLUMES FOR THE ANALYSIS OF ORGANIC COMPOUNDS: IMPROVING SUSTAINABILITY IN REMEDIATION

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INTRODUCTION

Much attention has been paid to improving the sustainability of remediation processes on site. What is often not considered is that laboratory services are an integral part of any site investigation or groundwater remediation project and yet the move to improving sustainability in these areas is relatively new. There have been significant benefits realised through reducing sample volumes including aspects of quality, OH&S, efficiency, reduction in carbon footprint and waste to landfill.

For organic analysis typically requested for site investigations or remediation, laboratories once typically required 500mL to 1L water samples. These were subjected to liquid/liquid extraction with methylene chloride (100–200 mL in total) followed by concentration of the extract to 1 mL for subsequent analysis via high resolution (capillary) gas chromatographic (HRGC) analysis typically with flame ionisation, electron capture or mass selective detections.

In early 2009 the Australian Environmental Division of ALS commenced a project with the aim of reducing the sample size required for routine analysis from (500–1000 mL) to 100 mL. The adoption of relevant practices and technologies enabled ALS to achieve this goal without compromising reporting limits. This project was completed nationally in 2009.

This presentation will outline the benefits of this strategy for the laboratory, its clients and the environment. Key areas of focus discussed include:

- Sample quality improvements (reduction in false positives/negatives)
- Field sampling efficiency improvements
- Manual handling improvements
- Reduction in freight volumes and carbon footprint
- Reduction in solvent usage (quantification of actual savings)
- Reduced RSI risks
- Reduction in waste to landfill

CONCLUSION

The movement to utilising smaller sample containers for standard SVOC analysis (e.g. TPH/TRH C10-C40, PAH/Phenols/OC/OP/PCB) has provided a multitude of benefits to industry and has improved efficiency and sustainability of practices.

REMEDIATION OPTIMISATION: OPERATION AND MONITORING OF ACTIVE REMEDIATION SYSTEMS AT REMOTE SITES

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INTRODUCTION

Operation of active remediation systems in remote areas of Australia can pose unique challenges. In the current backdrop of climate change and extreme variability in temperature and precipitation levels, further consideration must be given to optimising operation of remediation systems. PB has implemented an optimisation approach to address these challenges.

METHODS

Incorporation of optimisation techniques required pre-planning and was considered to be most effective during the design stage of projects. System optimisation opportunities have related to:

- Continuous monitoring and remote control over system operations
- SMS alerts to system shut downs
- Remote query and status of all critical devices
- Data logging and automated reporting
- Use of variable frequency drives in operating equipment
- Automated programming of active extraction points based on performance indicators

FINDINGS/RESULTS

Depending on the complexity of the programmable logic control (PLC) system associated with the remediation system (often associated with the number of phases, depth, and extent of contamination being recovered), development of a robust control system was found to represent a reliable method of maximising operational efficiency. Along with operational benefits, adopted optimisation methods and strategies resulted in cost and energy savings, reduced environmental impacts (and carbon footprint), and increased health & safety control.

CONCLUSIONS

Once installed, ongoing monitoring and review of remediation system operating parameters have been essential to optimising performance. Monitoring and analysis of data, trends, contaminant reduction indicators, and timely adjustments/modifications in response to real-time data were considered critical to optimisation of mass recovery efforts.

SUSTAINABLE MANAGEMENT OF CONTAMINATED SITES: EVALUATING THE CONTAINMENT OPTION

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SuRF Australia has prepared a draft Framework for Sustainable Remediation and Management of contaminated sites. These are consistent with a similar Framework prepared by SuRF UK. Preparing these Guidelines is an important step in advancing the management of contaminated sites in Australia, and will assist in providing a more consistent approach.

As outlined in the Guidelines, an important aspect of applying the principles of sustainability is to identify options for remediation and management that achieve an acceptable level of risk and are acceptable to the various stakeholders, and then evaluating them in terms of their environmental, economic and social benefits and effects. The Guidelines encourage taking a structured approach to identifying options, considering methods of remediation and management that can apply to source treatment, control of the pathways of exposure, and control of the receptors.

This paper considers the option of control of the pathways of exposure, particularly the option of containment of contamination. This option is widely applied in Australia, particularly where the contamination problem is large or difficult to address by other methods. However, to apply containment successfully requires careful consideration of the risk that the containment may fail, and confirmation that the containment will be successfully maintained as long as is required.

CRC CARE is carrying out a project involving the development of guidance on safe containment of contamination, and the guidance that has been prepared can be useful to consider.

The guidance is aligned to AS/NZS ISO 31000:2009 (Risk Management – Principles and guidelines), but specifically addresses the aspects of safe containment of contamination on sites. A draft set of guidelines has been prepared, and this paper will outline the key aspects of this guidance and how it can be applied. The descriptors for “likelihood” and “consequence” and the risk matrix are particularly important and will be documented, together with their calibration to confirm that the indicated risk and outcome is appropriate. Reference will also be made to related guidance that has been prepared and is being prepared by Australian State regulatory agencies.

REFERENCES

Reference will given to the current CRC CARE report on in-situ containment.

MANAGEMENT OF PHOSPHORUS IN ORGANIC AMENDMENTS FOR SUSTAINABLE PRODUCTION AND ENVIRONMENTAL PROTECTION

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Large quantities of organic amendments such as biosolids, poultry and animal manure and farmyard compost are added to soils to improve the physical, chemical and biological fertility of soils (Bulluck et al., 2002; Stark et al., 2007; Bolan et al., 2010). For example, in Australia, approximately 220,000 Mg (tonnes) of biosolids are produced annually, with 48% applied to agricultural land and the remainder is used in forestry, landfill and composting (Park et al., 2011). Confined animal production (i.e., beef and dairy cattle, poultry and swine) is the major source of manure byproducts in most countries. For example, of about 0.9 billion Mg organic and inorganic agricultural recyclable byproducts generated in US, approximately 45.4 million Mg are dairy and beef cattle manure, and 27 million Mg are poultry and swine manure (Walker et al., 1997; Bolan et al., 2004). These manure byproducts generate annually about 7.5 million Mg of N and 2.3 million Mg of P, compared to 9 million Mg of N and 1.6 million Mg of P that are applied to agricultural land in the form of commercial fertilizers. Similarly, in the United Kingdom, about 80 million Mg of livestock manures are collected from farm buildings and yards, requiring handling, storage and eventual application to the land. These manures contain about 450 000 Mg N, 119 000 Mg P and 330 000 Mg K with a potential monetary value of about £ 200 million per year (Smith et al., 2000). In addition to this, in situations where open grazing is practiced, large amounts of manure are directly deposited onto pasture land (Haynes and Williams, 1993).

The use of organic amendments in agriculture holds dual benefits for the waste producing industry and primary producers. For waste producing industries, land application provides a primary avenue for safe and beneficial recycling of these resource materials. For agricultural producers, these organic amendments are an alternative source of nutrients and have soil conditioning properties, thus the traditional routes of disposal for these valuable resources such as land-filling, incineration and ocean dumping are avoided. These organic amendments can also be used to enhance the rehabilitation of fragile disturbed lands such as mine sites (Seaker & Sopper, 1983; Park et al., 2011; Bolan et al., 2011).

Optimum use of these byproducts requires knowledge of their composition not only in relation to beneficial uses but also to environmental implications. Most of the environmental problems associated with land application of organic amendments have centered on the contamination of ground and/or surface water with two major nutrients, N and P (Sharpley et al., 2007). Unlike sewage sludge application, where land application is limited based on allowable metal loadings, regulations governing livestock and poultry manure byproducts are generally governed at the state level based on total N and/or P loading. Edwards and Someshwar (2000) have pointed out that “to reduce the risk of offsite contamination, land application guidelines should be developed that consider the total composition of the animal manure byproducts rather than only one component, i.e., N and/or P concentration”.

The application of organic amendments as a nutrient source is generally based on N input which is likely to provide more of other nutrients (especially P) than is required by crops. The potential for P surplus at the farm scale can increase when farming systems change from cropping to intensive poultry and animal production, as P inputs become dominated by poultry and animal feed rather than fertilizer. Cost-effective and innovative solutions are needed to expand the range of acceptable options in the management of nutrients, especially P in organic amendments. This will involve refining feed rations, using feed additives to increase P absorption, managing P in the manure, moving manure from surplus to deficit areas, finding alternative uses for manure, and targeting conservation practices to critical areas of P export during land application.

Several best management practices have the potential to reduce nutrients in runoff water and loading to surface waters (Sharpley *et al.*, 2007). They can be grouped into two broad categories: (1) technologies to reduce excessive nutrient levels in the soil, and (2) technologies to reduce discharges of nutrients via runoff or sediment loss from over-application of manure. For example, growing high biomass yielding plants can remove large amounts of nutrients and may be a promising remedial strategy to export and reduce excess soil nutrients. This paper gives an overview of various strategies used in managing P in organic amendments in relation to its disposal through land application with particular emphasis on potential for surface and ground water contamination.

REFERENCES

- Bolan, N.S., Park, J., Robinson, B., Naidu, R. and Huh, P. 2011. Phytostabilization: a green approach to contaminant containment. *Adv. Agron.* 112:146-204.
- Bolan, N.S., Szogi, A.A., Rothrock Jr., M.J. and Panneerselvam, P. 2010. Uses and Management of Poultry Litter. *World Poultry Science Journal* 66:673-698.
- Bulluck, L.R., Brosius, M., Ristaino, J.B. 2002. Organic and synthetic fertility amendments influence soil microbial, physical and chemical properties on organic & conventional farms. *Appl. Soil Ecol.* 19:147-160.
- Edwards, J.H. and Someshwar, A.V. 2000. Chemical, physical, and biological characteristics of agricultural and forest byproducts for land application. In: *Land Application of Agricultural, and Industrial By-products*, pp. 1-62. (Dick, W. A., Ed.) Soil Sci. Soc. Am. Madison, WI.
- Haynes, R.J. and Williams, P.H. 1993. Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Adv. Agron.* 49:119-199.
- Park, J.E., Choppala, G. and Bolan, N.S. 2011. Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *J. Haz. Mat.* 185:549-574.
- Seaker, E.M. and Sopper, W.E. 1983. Reclamation of deep mine refuse banks with municipal sewage sludge. *Waste Management & Research* 1:309-322.
- Sharpley, A.N., Herron, S. and Daniel T. 2007. Overcoming the challenges of phosphorus-based management challenges in poultry farming. *J. Soil & Water Conserv.* 58:30-38.
- Smith, K. A., Brewer, A. J., Dauven, A. and Wilson, D. W. 2000. A survey of the production and use of animal manures in England and Wales. *Soil Use Manage.* 16:124-132.
- Stark, C., Condrón, L.M., Stewart, A. and Di, H.J. 2007. Influence of organic and mineral amendments on microbial soil properties and processes. *Applied Soil Ecology.* 35:79-93.
- Walker, J.M., Southworth, R.M. and Rubin, A.B. 1997. U.S. Environmental Protection Agency regulations and other stake holders activities affecting agricultural use of by-products and wastes. In: *Agricultural Uses of By-products and Wastes*, pp. 28-47. (Rechcigl, J. E. and MaKinnon, H. C., Ed.) ACS, Washington, DC.

USE OF ALUM-DERIVED WATER TREATMENT SLUDGE TO REMOVE HEAVY METALS FROM AQUEOUS SOLUTIONS

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INTRODUCTION

Alum-derived water treatment sludge is a material deposited in large quantities in waste disposal areas in many parts of the world (Babatunde and Zhao, 2007). Indeed, alum [$\text{Al}_2(\text{SO}_4)_3$] is the most widely used coagulant in drinking water treatment (Faust and Aly, 1998). When added to water it flocculates as hydroxyl-Al species and results in coagulation of colloidal materials such as soluble organic matter and fine soil particles. Beneficial reuse of the material would reduce both the cost and need for disposal. The purpose of this study was to investigate the possibility of removing Cr(III), Cr(VI) and Pb(II) from aqueous solutions using alum water treatment sludge as an adsorbent.

METHODS

The sorption of Pb(II), Cr(III) and Cr(VI) from aqueous solution using alum-derived water treatment sludge, was investigated using the batch adsorption technique.

RESULTS AND DISCUSSION

The samples of sludge from two separate water treatment plants were used (one where alum was used alone and one where it was used in combination with activated C). X-ray diffraction analysis of samples revealed they both consisted of poorly crystalline, amorphous material. Adsorption of inorganic and organic species to the hydroxyl-Al polymers inhibits their crystallization (Haynes and Swift, 1989) and, as a result, the material had a very high BET surface area (i.e. 100-300 $\text{m}^2 \text{g}^{-1}$). The sorption characteristics of the two samples were generally very similar and adsorption capacity was strongly dependant on initial metal ion concentration, initial pH and dosage. Sorption isotherm data for all three ions fitted equally well to both Freundlich and Langmuir equations. Maximum sorption capacity and indices of sorption intensity both followed the order: Cr(III) > Pb(II) > Cr(VI). Kinetic data correlated well with a pseudo-second-order kinetic model suggesting the process involved was chemisorption. Sorption was pH-dependant with percentage sorption of Cr(III) and Pb(II) increasing from < 30% to 100% between pH 3 and 6 whilst that of Cr(VI) declined greatly between pH 5 and 8.

The ease and extent of desorption of metals from adsorbent surfaces is important since once the material becomes saturated with contaminated metals, and is no longer effective, it needs to be regenerated and reused (Zhou and Haynes, 2010). HNO_3 at a concentration of 0.1M was found to be effective at removing sorbed Cr(III) and Pb(II) from the sludge surfaces and regeneration was successful for eight sorption/desorption cycles.

CONCLUSIONS

It was concluded that water treatment sludge is a suitable material from which to develop a low-cost adsorbent for removal of Cr and Pb from wastewater streams.

ACKNOWLEDGEMENTS

Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE)

REFERENCES

- Babatunde A.O. and Zhao Y.Q. (2007) Constructive approaches toward water treatment works sludge management: an international review of beneficial reuses. *Crit. Rev. Environ. Sci. Technol.* 37: 129-164.
- Faust, D. and Aly, O. M. (1998) *Chemistry of Water Treatment*. Boca Raton, CRC Press.
- Haynes, R J and Swift, R.S. (1989) Adsorption of phosphate by aluminium-organic matter complexes as affected by pH and drying. *J. Soil Sci.* 40: 773-781.
- Zhou, Y-F. and Haynes, R. J. (2010) Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. *Crit. Rev. Environ. Sci. Technol.* 40: 909-977.

MOBILITY AND PHYTOAVAILABILITY OF COPPER IN THE PRESENCE OF RECYCLED WATER SOURCES

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INTRODUCTION

Recycled water irrigation provides a reliable source of water supply to farmers and also adds valuable plant nutrients and organic matter to the soil. However, untreated or partially treated wastewater can introduce inorganic and organic contaminants, including heavy metals, into agricultural land (Qishlaqi et al., 2008). The accumulation of copper (Cu) in the soil resulting from the long-term application of Cu fertilizers, recycled waters and sewage sludge could pose an environmental risk due to the downward mobility of Cu. Copper is an essential micronutrient for plant development when provided in trace quantities but at high levels it stunts plant growth or even cause death. Recycled water irrigation has also been shown to increase the amount of dissolved organic carbon (DOC) in soils either by acting as a source of DOC or by enhancing the solubilization of soil organic matter. The DOC has often been shown to influence the mobility and bioavailability of metal contaminants by forming soluble metal-DOC complexes (Bolan et al., 2011). In this study, the effect of recycled water sources on the mobility and phytoavailability of Cu was investigated. This study underpins the current trend in increased application of recycled water for plant production and unravels whether this practice influences Cu phytoavailability and also causes groundwater pollution.

METHODS

The impact of recycled water sources [farm dairy effluent (FDE), winery effluent (WE) and piggery effluent (PE)] on the mobility and phytoavailability of Cu was examined using two soils (Gawler-sandy loam and Adelaide Hills-silt loam) which varied in their texture, pH and organic matter content. The two soils were spiked with different concentrations (0, 100 and 500 mg kg⁻¹) of Cu added as copper nitrate which were incubated for a week at field capacity. After a week, the Cu-amended soils were further incubated with recycled water sources or MQ-water (as a control) for 3 months at field capacity. Sub-samples of these soils were used for leaching and phytoavailability experiments.

For the pulse-input leaching experiment, Cu spiked (100 and 500 mg Cu kg⁻¹ soil in the presence of recycled water sources or MQ water) soil samples were subsequently leached with Cu-free CaCl₂ solution. For the step-input leaching experiment, uncontaminated soil samples were leached with Cu spiked (100 mg L⁻¹) recycled water sources or CaCl₂ solution. The phytoavailability of Cu in the presence of recycled water sources was examined using Indian mustard (*Brassica juncea* var. Varuna) plants. The method devised by Stanford and Dement (1957) was used for the plant growth experiment. After harvesting plants, the roots and shoots were separated, washed with MQ water and the dry weight was recorded. The samples were then dried and ground to a fine powder for metal analysis. The ground plant material was digested with 5 ml of conc. HNO₃ and was analyzed for Cu using ICP-MS. The labile fraction of Cu was examined by monitoring the CaCl₂ extractable free Cu²⁺ in soils and pore water samples.

RESULTS AND DISCUSSION

The results from the leaching experiment suggested that the mobility of Cu was higher in soils incubated with recycled water sources than the soils treated in the presence of MQ

water (Fig. 1a and b). This is attributed to the formation of soluble Cu-DOC complexes. Copper leaching increased with increasing levels of Cu. With regard to pulse leaching, Cu concentrations were within the limit of irrigation water guidelines. In the step leaching process, the Cu in the leachates appeared faster in the soil columns leached with recycled water sources than MQ water. The DOC concentrations in the leachates increased with increasing levels of DOC in the recycled water sources. The DOC concentrations correlated positively with Cu concentrations in both step and pulse leaching.

The results from the plant growth experiment indicated that increasing the level of Cu applied through recycled water sources and MQ water elevated Cu concentration in plants. However, at the same level of Cu application, plants took up less Cu from recycled water-amended soils than from MQ-water amended soils (Fig. 1c). The effect was more pronounced in PE treated soils, with a reduction in Cu concentration in the plant tissues by 74.8% and 54% in GL soil, and 57.2% and 49% in AH soil at 100 and 500 mg kg⁻¹ Cu levels, respectively, compared to the Cu-spiked soils in the presence of MQ water. The recycled water sources significantly reduced the CaCl₂ extractable free Cu²⁺ in soils, indicating a decrease in the labile fraction of Cu.

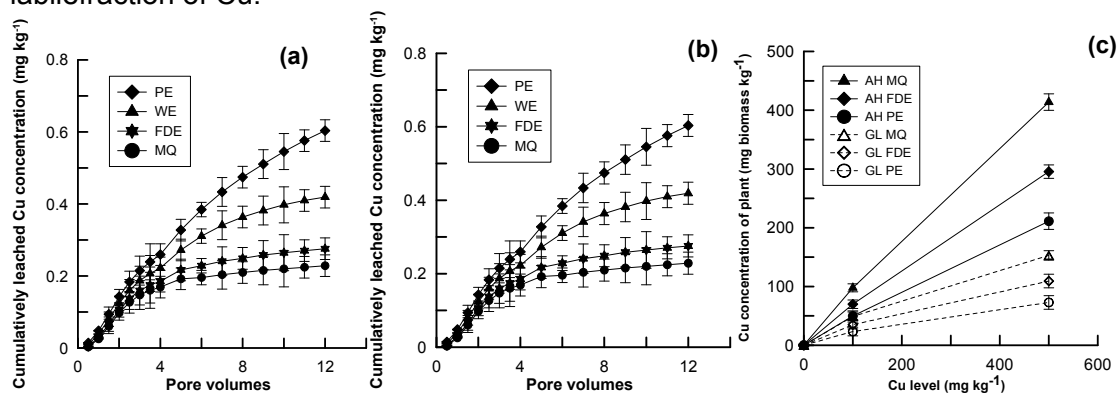


Fig.1. Cumulative Cu concentration of the pulse-input leachates in (a) Gawler soil (b) Adelaide Hills soil at 100 mg kg⁻¹ concentration and (c) concentration of Cu in plant at various levels of total soil Cu in the presence of MQ water and recycled water sources (FDE and PE) in Gawler (GL) and Adelaide Hills (AH) soils.

CONCLUSIONS

The results clearly showed that the presence of DOC in the recycled water was proved to be effective in reducing Cu phytotoxicity at high levels of Cu addition, indicating that the Cu-DOC complexes decreased the bioavailability of Cu to plants. While the leaching of Cu increased with increasing levels of Cu, it depended on the extent of Cu adsorption and formation of soluble Cu-DOC complexes.

REFERENCES

- Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, T., McDowell, R., Senesi, N. (2011) Dissolved organic matter: biogeochemistry, dynamics and environmental significance in soils. *Adv. Agron.* 110: 1-75.
- Qishlaqi, A., Moore, F., Forghani, G. (2008) Impact of untreated wastewater irrigation on soils and crops in Shiraz suburban area, SW Iran. *Environ. Monit. Assess.* 141: 257-273.
- Stanford, G., DeMent J.D. (1957). A method for measuring short-term nutrient absorption by plants: 1. Phosphorus. *Proc. Soil Sci. Soc. Am.* 21:612-617.

SUBSTRATE-SPECIFIC SOLAR LIGHT PHOTOCATALYTIC ACTIVITY OF TITANIA PRODUCED FROM Ti-SALT FLOCCULATED SLUDGE

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INTRODUCTION

Titania photocatalyst was produced by calcination of Ti-salt flocculated sludge with wastewater and its physicochemical properties were investigated. Previous studies dealt with titania from sludge used one test substrate under UV light irradiation and claimed the high photocatalytic activity of titania was extended to other substrates (Shon et al., 2007; Okour et al., 2010). However, according to the literature, the photocatalytic activity is substrate-specific; consequently, applying a single substrate test does not represent the whole photocatalytic activity for a given photocatalyst (Ryu and Choi, 2008) and utilizing the whole solar light spectrum rather than a small fraction of sunlight corresponds to UV region is environmentally needed in practical applications. Therefore, the objectives of this study are: i) to use various substrates such as phenols, alcohols, herbicides, dyes and humic acids which have different structures and molecular properties to establish substrate-specific activity of titania from sludge; ii) to investigate the possibility of using titania under solar light; and iii) to compare the solar photocatalytic activity of titania with the most widely used photocatalyst (Degussa TiO₂-P25).

METHODS

TiCl₄ flocculation of biologically treated sewage effluent withdrawn at Sydney Olympic Park wastewater treatment plant, Australia was carried out. The collected sludge after TiCl₄ flocculation was dewatered then dried at 100°C for 12 hr. The dried sludge was grinded and incinerated at 600°C for 12 h. Titania photocatalyst produced from the sludge was washed with deionised water for three times and finally dried in an oven at 100°C for 5 hr. The photodegradation process was carried out using artificial solar light system. Titania photocatalyst was dispersed into distilled water at fixed concentration of 0.5 g/L. An aliquot of phenols, alcohols, herbicides, dyes and humic acids stock solution was subsequently added to the solution to give a desired substrate concentration of 10 mg/L. After that, the solution was stirred for 60 min to allow the equilibrium of adsorption and desorption. At appropriate time intervals, 20 mL of the solution was collected and filtered with 0.45 µm membrane. The photodegradation values were determined using UV-vis spectrophotometer and dissolved organic carbon (DOC) analyser and the ratios of photodegradation values were plotted against time to obtain the percentage of photodegradation rate.

RESULTS AND DISCUSSION

Results indicated that titania from wastewater sludge was a substrate-specific photocatalyst with different photocatalytic degradation rates of test substrates under solar light. Titania showed a high photocatalytic degradation rate for dyes and a moderate degradation rate for humic acids, alcohols and herbicides, while phenols had the lowest degradation rate. The difference in the photocatalytic degradation rates amongst the substrates used might be related to the difference in the mechanism of the photocatalytic degradation of each substrate due to the physiochemical interactions between titania and various substrates. Specific-substrate titania from sludge showed higher photocatalytic degradation rates on

herbicides and alcohols among the five tested substrates compared with Degussa TiO₂-P25. These findings confirmed the highly substrate-specific activity of titania from sludge and Degussa TiO₂- P25 in which each photocatalyst showed different photocatalytic degradation rates using different substrates.

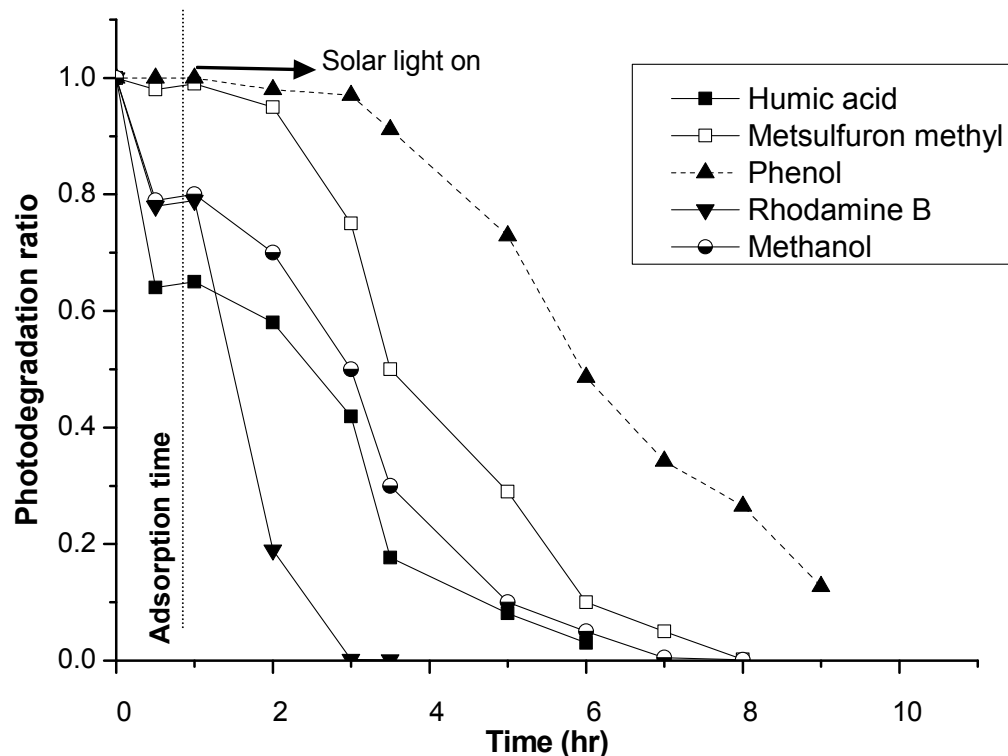


Fig. 1. Substrate-specific photocatalytic activity of titania from sludge under solar light.

CONCLUSIONS

Titania from wastewater sludge, as a specific-substrate photocatalyst, showed different photodegradation rates of test substrates under solar light irradiation depending on the photocatalysis mechanism between titania and the test substrates. Titania exhibited high photocatalytic degradation rates for some substrates when compared with TiO₂-P25 and indicated the specific-substrate behaviour of titania photocatalyst.

REFERENCES

- Shon, H. K., Vigneswaran, S., Kim, I. S., Cho, J., Kim, G. J., Kim, J. B., Kim, J.-H. (2007) Preparation of titanium dioxide (TiO₂) from sludge produced by titanium tetrachloride (TiCl₄) flocculation of wastewater. *Environ. Sci. Technol.* 41: 1372-1377.
- Okour, Y., Shon, H.K., El Saliby, I.J., Naidu, R., Kim, J.B., Kim J.-H. (2010) Preparation and characterisation of titanium dioxide (TiO₂) and thiourea-doped titanate nanotubes prepared from wastewater flocculated sludge. *Bioresource Technology.* 101: 1453-1458.
- Ryu, J., Choi, W. (2008) Substrate-specific photocatalytic activities of TiO₂ and multi-activity test for water treatment application. *Environ. Sci. Technol.* 42: 294-300.

UTILIZATION OF DISTILLERY EFFLUENT FOR FERTIGATION OF SUGARCANE

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INTRODUCTION

Molasses, a by-product of sugar industry is used to produce ethanol. With around 319 distilleries producing over 3 gigalitres of alcohol, 400 gigalitres of wastewater is generated each year in India (Uppal, 2004). The wastewater generated (also called Spentwash) has very high biological oxygen demand (BOD) and chemical oxygen demand (COD), is rich in N, P, K, Ca, S, micronutrients and organic matter, and cannot be directly disposed-off in water bodies. Land application of spentwash is a suitable option for prevention of pollution of water bodies and maintenance of soil fertility (Suganya and Rajannan, 2009). The present investigation was carried out to monitor the effect of pre-sown and standing crop application of distillery effluent vis-à-vis fertilizer application on yields of sugarcane-ratoon-ratoon system and changes in the soil properties.

METHODS

The distillery effluent used in the study had 8.24 pH, 2767 $\mu\text{S cm}^{-1}$ EC at 25°C, 16640 mg total solids, 7313 mg total suspended solids, 9327 mg total dissolved solids, 3805 mg BOD, 10400 mg COD, 59.4 mg N, 536 mg K and 216 mg Na L⁻¹ effluent. A field experiment was conducted at Gajraula, India. Surface (0-15 cm) soil of the experimental site had sandy loam texture, 6.36 pH and 0.109 dS m⁻¹ EC at 25°C (1:2 soil water), 7.1 g OC kg⁻¹ soil, 267.6 kg alkaline KMnO₄ hydrolysable N, 43.9 kg Olsen's P₂O₅ and 188.9 kg exchangeable K₂O ha⁻¹. The treatments were imposed in split plot design in triplicate and unit plot size of 8 m × 3.5 m. The treatments consisted of main plots: control (all irrigations with tube-well water) (I₀), first pre-sowing irrigation with undiluted effluent and subsequent irrigation with tube-well water (I₁), one irrigation with effluent: tube-well water flow rate (1:3) at tillering stage and rest all irrigations with tube-well water (I₂), two irrigations with effluent: tube-well water flow rate (1:4) at tillering and 30 d after tillering stage irrigation and rest all irrigations with tube-well water (I₃). The subplots either received no fertilizer application (F₀) or had 50 % of recommended dose (50 kg N, 60 kg P₂O₅ and 40 kg K₂O ha⁻¹ as basal dose in the form of urea, DAP and MOP (F₁) and top dressing of 50 kg N ha⁻¹ at tillering and in June before the onset of monsoon). Nitrogen to ratoon crops was applied in three equal splits, i.e. after harvesting of main crop and in April and June. At maturity, canes were harvested and yields of millable cane were recorded from each plot. Sucrose (%) in canes of each plot was also estimated. Soil samples collected at 0-15, 15-30, 30-45 and 45-60 cm after second ratoon were analysed for different soil parameters.

RESULTS AND DISCUSSION

In general, application of 50% recommended fertilizer dose increased the cane yields under different effluent treatments (Fig 1). Use of distillery effluent irrespective of the method of application significantly increased the cumulative yields of sugarcane over no application of effluent; however, the differences among effluent treatments were statistically not significant. Suganya and Rajannan (2009) reported that method of application of distillery spentwash

(pre-sown or post-sown) had no significant effect on yields of maize. The effect of different treatments on sucrose (%) of the main as well as first and second ratoons crops was statistically not significant (data not presented)

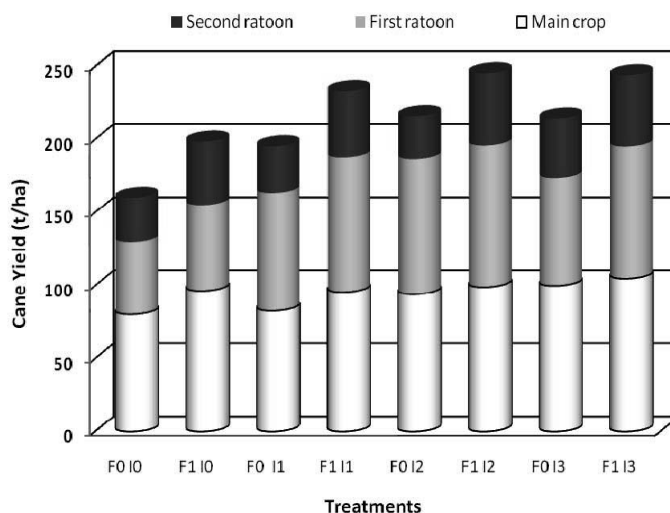


Fig 1. Effect of different treatments on cumulative cane yields of main crop, first ratoon and second ratoon.

After the harvest of second ratoon crop, no significant effect of different treatments was noted on soil pH, EC, organic C, exchangeable Na and Olsen's P; however, relatively higher build-up of EC and organic C in surface soil (0-15 cm) was noted in I_2 treatment. With no fertilizer application, both I_1 (318 kg N ha⁻¹) and I_2 (345 kg N ha⁻¹) significantly increased accumulation of available N as compared to I_0 (238 kg N ha⁻¹) in 30-45 cm layer. Significantly higher accumulation of available K was recorded in surface (0-15 cm) soil under I_2 (1231 kg K ha⁻¹) and I_3 (870 kg K ha⁻¹) as compared to I_0 (451 kg K ha⁻¹). With no fertilizer application, significantly higher accumulation of available K was recorded in 15-30 cm under I_2 (1199 kg K ha⁻¹) and I_3 (1153 kg K ha⁻¹) compared to I_0 (303 kg K ha⁻¹). Further, significantly higher accumulation of available K was recorded in 30-45 cm soil under I_1 (972 kg K ha⁻¹), I_2 (1195 kg K ha⁻¹) and I_3 (876 kg K ha⁻¹) compared to I_0 (384 kg K ha⁻¹).

CONCLUSIONS

Distillery effluent had favourable effect on cumulative cane yields. Effluent irrigation had potential to cut down the fertilizer consumption of the farmers by fifty per cent. Under good soil drainage conditions, application of distillery effluent as pre-sown irrigation with undiluted effluent (I_1) or one irrigation with (1:3) diluted effluent (I_2) or two irrigations with (1:4) diluted effluent (I_3) helps building up the fertility status of the soil.

REFERENCES

- Uppal, J. (2004) Water utilization and effluent treatment in the Indian alcohol industry-an overview. In: Liquid Assessts, Proceedings of Indo-EU workshop on promoting efficient water use in agro-based industries. TERI Press, New Delhi, India, pp.13-19.
- Suganya, K. and Rajannan, G. (2009) Effect of onetime post-sown and pre-sown application of distillery spentwash on the growth and yield of maize crop. *Bot. Res. Intl.* 2: 288-294.

PHYTOCAPPING: AN ALTERNATIVE TECHNOLOGY FOR THE SUSTAINABLE MANAGEMENT OF LANDFILL SITES

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INTRODUCTION

Despite our increasing ability and efforts to recycle and reuse materials and resources, landfill remains the final repository for many different types of waste. In Australia, 50% to 60% of the Municipal Solid Waste (MSW) is placed in landfills (El-Fadel and Massoud, 2000). It is estimated that an excess of 2000 landfill sites exist in Australia with > 520 in Victoria, > 300 in New South Wales, 460 in South Australia and 309 in Western Australia, although numerous local communities operate small landfill sites. Xu et al. (1999) reported that the landfill area in Brisbane, Adelaide, Melbourne and Sydney ranged from 12 to 100 ha, with a median of 35 ha. The modern trend of landfilling is to position, design and construct larger landfills further away from suburban areas, with multiple transfer stations servicing them (Xu et al., 1999). Consideration of an appropriate site for positioning landfill has rarely considered the growth of urban areas in the future or the true costs of landfill. This paper describes the concept of Phytocapping and future areas of research in this area.

PHYTOCAPPING TECHNOLOGY

Conventional capping technologies are now accepted to be increasingly ineffective with time. Thus, cost-effective alternative systems are of increasing interest, including the use of plants to control and limit water entry into waste, otherwise known as Phytocapping. Examples of Phytocapping designs are shown in Figure 1. Phytocapping reduces percolation through three main mechanisms (1) canopy interception of rainfall, (2) storage of moisture in the soil layers and (3) evapotranspiration of stored water. From a comprehensive review of literature, the major findings and future areas of research include:

- Tree species or deep rooted grasses that are able to access the full storage layer depth have an advantage in phytocap designs.
- Stemflow and preferential flow paths are potential problems for the mitigation of percolation through landfill caps. Further research over long time frames in phytocaps is needed. However, stemflow tends to contribute small amounts of water transport. Studies on phytocaps from the US have reported that phytocaps generally transmit less percolate than conventional caps. Design of the storage layer is site specific (i.e. climate, soil) and critical in the success of the capping system.
- Data reported over past several decades have indicated an inability of plant roots to rupture and penetrate compacted clay or other synthetic lining materials.
- Irrigation with saline and sodic landfill leachate has been shown to impact physical properties of soils.
- Landfills contain putrescible wastes that degrade and produce landfill gases when they come in contact with water. Modern landfills collect and combust a substantial proportion of the gas, predominantly CH₄. However, CH₄ still diffuses through the cap. Methanotrophic microbes are known to oxidize CH₄ to CO₂ and H₂O. Several factors influence the efficiency of oxidation, including soil moisture, aeration and nutrient status. Oxidation of CH₄ and other contaminants may be enhanced by increasing aeration and

the supply of nutrients. The beneficial role that organic amendments play in phytocapping technology needs further attention.

- Further work needs to be conducted on the application of high energy plantations as phytocapping plant species. Many species currently under study for bioenergy crops are robust, able to tolerate a wide range of stresses and have deep root systems.
- The interaction between microbial communities associated with rhizosphere soils for enhancement of CH₄ oxidation, and co-metabolism of other volatile species (e.g. trichloroethylene) diffusing through cap soils needs further research. High biomass plants proposed as bioenergy crops in particular have received insufficient research to date.
- Although many modern landfills design a layer of loamy and organic dressing material, many older and poorly designed landfills possess poor soil attributes, such as high clay, low aeration etc.

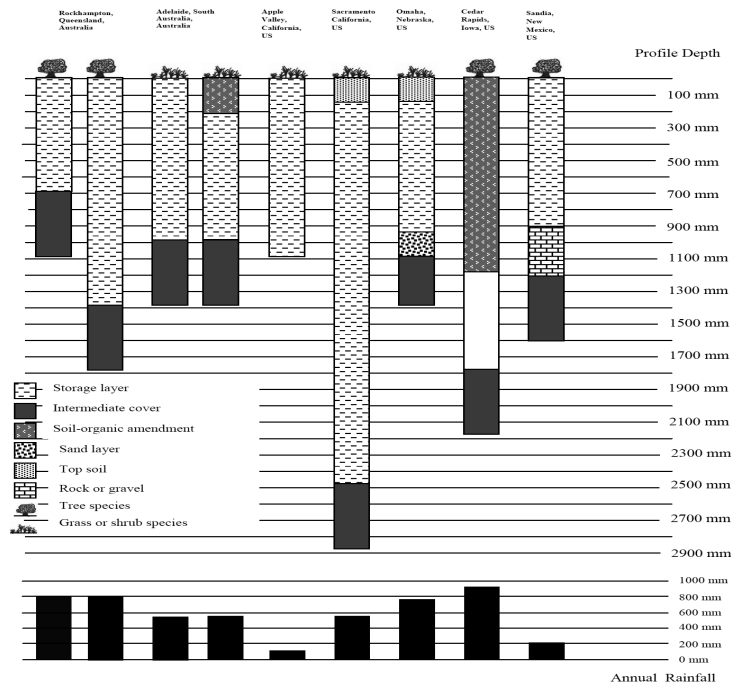


Figure 1. Profiles of Phytocaps reported from the United States and Australia demonstrating variations in design, including average rainfall data for the local area.

CONCLUSIONS

Phytocapping has been shown to be at least as effective as clay capping in reducing percolation through landfill cover materials, and adding many additional benefits, including increased cap stability, reduced erosion of capping materials and wind-blown dust, enhanced methane oxidation from microbial communities. There is considerable potential for high biomass energy plants, however further work is need in this area.

REFERENCES

- EL-FADEL, M. & MASSOUD, M. 2000. Emissions from landfills: A methodology comparative assessment. *Environmental technology*, 21, 965-978.
- XU, X., RUDOLPH, V. & GREENFIELD, P. F. 1999. Australian urban landfills: management and economics. *Waste Management Research*, 17, 171-180.

LANDFILLS: SUSTAINABILITY COSTS AND CHALLENGES OF WASTE MANAGEMENT

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INTRODUCTION

There is an extensive body of literature on the direct costs and particular technological challenges of minimising landfill impacts on the environment – specifically through containment of contamination and then remediation. The Commonwealth Government's current *National Waste Policy* has been informed by the literature and aims to avoid the generation of waste, reduce the amount of waste (including hazardous waste) for disposal, manage waste as a resource, ensure that waste treatment, disposal, recovery and re-use are undertaken in a safe, scientific and environmentally sound manner, and contribute to the reduction in greenhouse gas emissions, energy conservation and production, water efficiency and the productivity of the land. However, like other reports (e.g. RPM *et al.*, 2001), it is clear that the full sustainability costs and challenges of waste disposal have further to be researched. In this study, the current sustainability challenges have been reviewed, as well as the emerging trends in sustainability frameworks for waste management, the technologies and systems for resource recovery and disposal, the sustainable initiatives for managing waste as a resource, and setting up the argument for why an integrated resource planning framework approach is useful for waste management in Australia.

PROJECT SCOPE

This project builds upon on previous waste management studies and reports. The *National Waste Report 2010* (Commonwealth, 2010), *Beyond Recycling* (ISF, 2004) and many others provided the basis for understanding and critiquing waste management in Australia today, and the impacts and opportunities available. The study involved a critical literature review, stakeholder consultation, policy analysis and presents a new framework for integrated resource planning, that enables the lowest cost options for avoiding waste to landfill be determined. to the whole of society This framework considers all sustainability costs (economic, social, environmental), takes a whole-of-community approach to landfills and their impacts, while allowing long-term sustainability to be considered. Three immediate dimensions – sustainability costs, responsibility and time were developed (Figure 1).

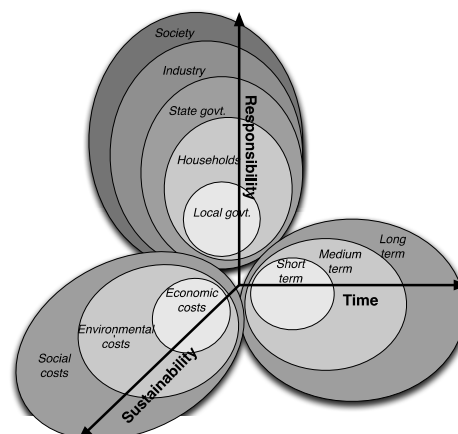


Figure 1. Sustainable waste management dimensions

DISCUSSION AND CONCLUSIONS

To date, many landfill analyses have used a narrower framework and have focused on specific technologies, rather than considering the full suite of measures and policy instruments available. Further, various environmental and social costs are often excluded from analyses due to the difficulty in quantifying these indirect costs. If all direct and indirect costs are included and the whole production and consumption chain is examined, within a consistent framework, what is discovered is the lower costs options that achieve the greatest sustainability outcome. Understanding the true cost to the community of waste disposal and identifying who currently pays (table 1) allows the disparate range of waste management options available – from AWTs to investment in waste avoidance – to be compared on an equal basis. Further costs can be redistributed to ensure more equitable responsibility, consistent with the principles of Extended Producer Responsibility.

Table 1. Sustainability cost matrix of waste disposal to multiple stakeholders

Sustainability costs	Scale		Stakeholder (who pays)			
	Local	Global	Local council	Residents	Govt	Society
Environmental costs	<ul style="list-style-type: none"> Leachate Toxic substances/contamination 	<ul style="list-style-type: none"> Climate change Energy scarcity Peak phosphorus 	x	x	x	x
Economic costs	<ul style="list-style-type: none"> Transport costs (fuel, vehicle maintenance, road repair/upkeep) Reaching capacity Capital Remediation M & E 	<ul style="list-style-type: none"> Fuel costs Market fluctuations 	x	x	x	
Social costs	<ul style="list-style-type: none"> Liveability (noise, aesthetics, increased traffic,) Vermin Odour Illegal dumping Real estate value 		x	x		x

This integrated resource planning approach has been undertaken in the water and energy conservation sectors respectively with win-win results for industry and the community. By analysing the entire waste production chain in consultation with all key stakeholders, more informed, appropriate and effective decisions can be made to better manage waste in Australia.

REFERENCES

- Institute for Sustainable Futures (2004) *Beyond Recycling: An Integrated Waste Management Framework for Local Government, Part A: Developing an integrated waste management strategy and empowering the community*, for the Local Government Association of NSW & Shires Association of NSW.
- Commonwealth of Australia (2010) *National Waste Report 2010*. Department of the Environment, Water, Heritage and the Arts, Canberra.
- RPM Pty Ltd, Kenney Lin & Associates, and Energy Strategies Pty Ltd (2001) *The Actual Costs of Waste Disposal in the ACT*, prepared for the ACT Waste Department of Urban Services, ACT.

USE OF ORGANIC AMENDMENTS AND RESIDUE MUD TO IMPROVE THE PROPERTIES OF BAUXITE RESIDUE SAND AS A GROWTH MEDIUM

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INTRODUCTION

Bauxite ore is mined and then refined using the Bayer process in which Al-containing minerals are dissolved in hot NaOH. For each tonne of alumina, 1-2 tonnes of insoluble solids (bauxite processing residue) are produced and these are usually deposited in impoundments surrounding the refinery (Jones and Haynes, 2011). At Alcoa, processing residue is separated into residue mud (< 150 µm) and residue sand (> 150 µm). The residue sand is used to construct the outer embankments of residue storage areas and the residue mud (after dewatering/thickening and direct carbonation with CO₂) is deposited within them (Cooling, 2007). The storage area is built in a progressive stack and periodically the perimeter embankments are built higher with sand and the volume within is then filled with mud.

The residue sand in the outer walls of embankments is amended with gypsum and fertilizers and progressively revegetated with ground covers, bushes and trees native to a West Australia sand dune system (e.g. Golden Wreath Wattle; *Acacia saligna*). Growth of these plants is often disparate, sometimes poor and there is little regeneration of the vegetation. In order to control dust, the inner embankment walls are sown with Wimmera ryegrass (*Lolium rigidum*). Previous research has suggested that additions of organic wastes/composts either alone (Jones et al., 2010) or in combination with small amounts of residue mud (Jones et al., 2011) can improve the chemical, microbial and particularly physical properties of residue sand and that such additions are likely to improve the ease of rehabilitation/revegetation. The purpose of this study was to compare the effects of the addition of residue mud (neutralized by either direct carbonation or seawater treatment), either alone or in combination with green waste compost, on chemical, physical and microbial properties of residue sand and on plant germination in the treatments.

METHODS

The effects of addition of carbonated residue mud (RMC) or seawater neutralized residue mud (RMS), at two rates, in the presence or absence of added green waste compost, on the chemical, physical and microbial properties of gypsum-treated bauxite residue sand were studied in a laboratory incubation study. The growth of two species commonly used in revegetation of residue sand (*Lolium rigidum* and *Acacia saligna*) in the treatments was then studied in an 18-week greenhouse study.

RESULTS AND DISCUSSION

Addition of organic residues (composts, manures) improved fertility (supply of N, P, K, Mg and micronutrients), physical (meso- and micro-porosity, available water holding capacity and volume of water held at field capacity) and microbial properties (size and activity of the soil microbial community). Addition of residue mud tended to increase EC, soluble and exchangeable Na and HCO₃⁻ alkalinity (carbonated mud had a greater effects than seawater neutralized mud) but both materials improved physical conditions (increased meso- and

micro-porosity). They also tended to induce aggregation of sand particles to form the beginnings of a soil structure. A combination of organic residue plus residue mud had an additive effect on improving physical and microbial properties. The increased size and activity of the microbial community was attributed to aggregate formation induced by addition of the two materials together. In agreement with visual observations at the site, Wimmera ryegrass grew reasonably well in gypsum/fertilizer-treated residue sand with or without additions of mud and/or organic amendments. By contrast, *A. saligna* was not well adapted to grow in gypsum-treated sand and addition of compost greatly promoted its growth. This was attributed to the large inputs of K in the compost which partly alleviated the negative effect of high solution Na on plant growth. Addition of carbonated mud had a much more detrimental effect on *A. saligna* growth than seawater-neutralized mud and this was attributed to the greater alkalinity and HCO_3^- content of the carbonated mud.

CONCLUSIONS

Whilst both *L. rigidum* and *A. saligna* are known to be well-adapted to saline-sodic soils, it is evident that *A. saligna* is not well equipped to grow in gypsum-treated residue sand. There is a need to investigate whether this is true for other native species used in revegetation since this would, at least partially, explain their poor performance in the residue sand. Addition of compost to the residue sand not only improved soil physical conditions, increased soil microbial activity and raised macro- (N, P, K, Ca) and micronutrient (Zn, Fe, Mn) status, but the substantial additions of K and Mg apparently alleviated the negative effects of high solution Na on growth of *A. saligna* and therefore greatly promoted plant growth. The findings of this study has provided important information on the conditions of residue sand that need to be developed prior to establishing rehabilitation at Alcoa's residue storage areas.

REFERENCES

- Cooling, D.J. (2000) Improving the sustainability of residue management practices – Alcoa World Alumina, In: Fourie, A.B., Jewell, R.J. (Eds.) *Paste 2007 – Proceedings of the Tenth International Seminar on Paste and Thickened Tailings*, Australian Centre for Geomechanics, Perth, Australia, pp. 3-15.
- Jones, B.E.H. and 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.
- Jones, B.E.H., Haynes, R.J. and Phillips, I.R. (2010) Effect of amendment of bauxite processing sand with organic materials on its chemical, physical and microbial properties. *J. Environ. Manag.* 91: 2281-2288.
- Jones, B.E.H., Haynes, R.J. and Phillips, I.R. (2011) Influence of organic waste and residue mud additions on chemical, physical and microbial properties of bauxite residue sand. *Environ. Sci. Pollut. Res.* 18: 199-211.

ANALYSIS OF PCBs IN BIOSOLIDS & OTHER WASTE MATERIALS

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INTRODUCTION

Biosolids are a mix of water and organic matter that are byproducts of sewage treatment processes. The waste comes from humans and industry with most derived from household, kitchens, laundries and bathrooms. Biosolids are treated in a way to eliminate health risks and improve beneficial characteristics.

Australia produces about 450000 tonnes per year of biosolids when reported on a dry weight basis (ANZ Biosolids Partnership, Biosolids Guidelines Dec 2009). Most biosolids are used on farmland as a fertiliser and a small percentage for other uses such as composting. Biosolids contain beneficial macronutrients but may also contain levels of arsenic, cadmium, lead, OC pesticides, PCBs which limit their use. State regulators set *Contaminant Acceptance Concentration Thresholds*. In the case of NSW, the guidelines are set by the *Office of Environment & Heritage* where the class of biosolid is based on the levels of metal and organic chemical contaminants and on the treatment processes to reduce pathogen levels, vector attractants and odour. In NSW (and most states) the Acceptance concentration threshold for Polychlorinated biphenyls (PCBs) for Grade A classification of biosolids is 0.3 mg/kg (on a dry weight basis).

This presentation will focus on the analytical challenge of determining PCBs in biosolids and other complex matrices. Polychlorinated biphenyls are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings. PCBs were widely used for many applications, especially as dielectric fluids in transformers, capacitors, and coolants. Due to PCB's toxicity and classification as a persistent organic pollutant, PCB production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001.

Testing of complex waste samples such as biosolids for PCBs down to below 0.3 mg/kg raises a number of analytical challenges –

- (1) The threshold value of 0.3 mg/kg is based on dry weight and some biosolids have water levels of 80% or higher. On an as received basis, this equates to the laboratory needing to detect below 0.06 mg/kg.
- (2) The Biosolids Guidelines are based on PCB Aroclors rather than individual congeners. The Aroclor method requires chromatographic pattern matching to a commercial aroclor. In the case of biosolids, microbiological activity and weathering causes degradation of the lighter congeners resulting in a difficult process to match aroclors.
- (3) Biosolids and other waste materials have an extremely high organic content which produces high levels of chromatographic interference. The extracts require extensive cleanup and/or highly selective detectors to produce accurate results.

The National Measurement Institute, Pymble Organics Laboratory has traditionally analysed Organochlorine compounds such as PCBs using Gas Chromatography with electron capture detector (GC-ECD). Recently we have started to employ GC Tandem MS techniques to this detection challenge.

METHODS

A portion of biosolid or waste material is extracted using a mix of hexane:acetone. The extract is cleaned up using Gel Permeation Chromatography, acid cleanup and/or sulfur removal processes before conducting GC-ECD or GC Tandem MS analysis. Spikes, duplicates and blanks are included in batches to ensure internal quality control.

RESULTS AND DISCUSSION

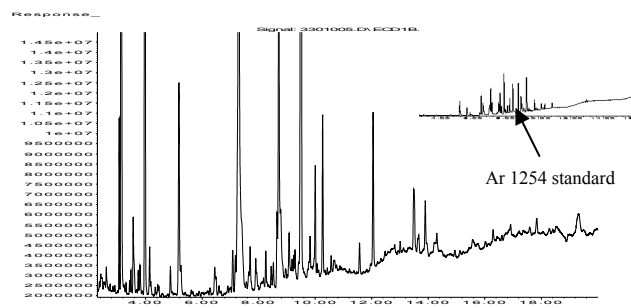
NMI has developed a technique to determine PCBs as Aroclors in waste materials & biosolids using GC Tandem MS. The precision data for GC Tandem MS determination of spiked Aroclor 1260 in waste material is presented in Table 1. Figure 1 also gives a chromatographic comparison of GC-ECD analysis and GC Tandem MS determination of Aroclors in a biosolid material. The figure indicates that for this analysis, the GC-ECD has a very complex chromatogram making PCB determination very difficult. The GC Tandem MS chromatogram allowed a greatly improved identification of contaminant Aroclors (in this case, Aroclor 1254).

Table 1. Precision data for waste samples spiked with 1 mg/kg Aroclor 1260.

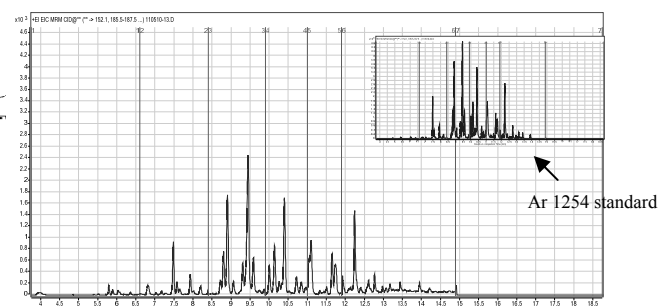
Analyte	Calculated concentration of replicated spike samples (n) (mg/kg)							Mean Conc.	% RSD	Mean Percentage Recovery (%)
	1	2	3	4	5	6	7			
PCB 1260 total	1.30	1.14	1.36	1.00	1.06	1.26	1.22	1.19	11	119

Figure 1. (A): GC-ECD chromatogram of biosolid sample containing Ar1254. (B): GC Tandem MS MRM chromatogram of same biosolid sample with Ar1254 identified.

(A) GC-ECD chromatogram



(B) GC Tandem MS MRM Chromatogram



CONCLUSIONS

The use of GC Tandem MS has simplified the detection of PCBs in complex matrices such as biosolids and waste materials. The NMI Pymble Organics laboratory has employed this technique on a range of highly complex samples and we have concluded that GC Tandem MS is an invaluable tool for trace organochlorine detection.

REFERENCES

- Australia & New Zealand Biosolids Partnership, "Review of Biosolid Guidelines – Summary" Dec 2009.
- Environmental Guidelines, "Use and Disposal of Biosolids Products", NSW EPA Dec 2000.
- Porta M, Zumeta E. Implementing the Stockholm treaty on POPs [Editorial]. Occupational & Environmental Medicine 2002; 59: 651-652.

METAL SPECIATION AND DISTRIBUTION IN BIOSOLIDS

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INTRODUCTION

Biosolids (i.e. stabilized sewage sludge) are continuously produced as a by-product of municipal wastewater treatment and their subsequent disposal presents a major management issue for the wastewater industry. Among the disposal options for biosolids application to land as a soil conditioner is of major importance. Nevertheless, the land application pathway has recently been subject to widespread scrutiny due to uncertainties regarding the long term fate and release of contaminants from sludge-derived products. The inevitable presence of metal contaminants in biosolids is of particular concern due to their accumulative and persistent nature in the environment. Despite this, knowledge of the factors controlling metal bioavailability in biosolids and biosolids-amended soils remains far from complete. For instance, although it is well known that metal contaminants in sewage sludge can potentially be sorbed by both inorganic and organic constituents, the nature of the key metal sorbing phases is still a matter of debate. While some authors have suggested that organic matter is the dominant sorbent (Beckett et al., 1979) others have indicated that inorganic constituents such as iron and manganese oxides play the dominant role. If the dominant sorptive phase is indeed organic matter, mineralisation processes may lead to contaminants being released from the biosolids over time. This possibility has prompted various authors (Beckett et al., 1979) to advance a 'time bomb' hypothesis by which a long-term increase in contaminant bioavailability is envisaged. On the other hand, if the contaminants are mainly sorbed by stable inorganic constituents it is feasible that substantial changes in their long-term bioavailability may not occur. To date, evidence in favour of either hypothesis is inconclusive (e.g. Hettiarachchi et al. 2006). In fact, very little research has actually been conducted to systematically assess the partitioning of biosolids contaminants between the organic and mineral sludge phases. Yet this knowledge would be invaluable for predicting the long-term effects of land application and associated risks, and could also potentially advance efforts to maximise stable associations of contaminants in sewage sludge derived end-products.

The primary objective of the study described here was to make use of a variety of techniques including advanced spectroscopic techniques specifically suited to the analysis of key biosolids constituents and the interrogation of mechanistic factors.

METHODS

The biosolids samples were sourced from secondary wastewater treatment plants in Australia. Three of these biosolids were sampled straight from the sludge dewatering stage of secondary treatment systems and are referred to as 'fresh' biosolids, while the remaining three were obtained from drying beds and/or composting stockpiles and are referred to as 'aged' biosolids. In additions, 'historical' biosolids used in long terms field trails in the US and UK were studied. The biosolids were chemically characterized for pH, metal and organic matter content. Furthermore, the organic and inorganic fractions were separated on the basis of difference in specific gravity using a polytungstate solution. Metals in the two fractions were determined by ICP-MS after acid digestion. Double-polished thin sections of embedded biosolids were used to collect μ -XRF elemental maps at the XFM beamline, Australian Synchrotron. This beamline is equipped with a Maia 384 element detector which allows collection times in the order of a few ms per pixel. This allowed maps of 4x4mm to be collected in approximately 3 hours with a lateral resolution of 2 μ m. Furthermore, bulk EXAFS

spectra of Cu and Zn were collected for the same biosolids at the ANBF beamline, Photon Factory, Japan.

RESULTS AND DISCUSSION

The Cu and Zn EXAFS spectra of the fresh biosolids were clearly different from those of the biosolids that were stockpiled (aged biosolids). Analysis of the results by Linear Combination Fitting (LCF) indicated that sulfide minerals play a significant role in metal binding in fresh biosolids. In particular, the presence of a large proportion of Cu(I) sulphides was noted. However, the role of sulfides as the primary metal sink is replaced in the aged biosolids by the increasing contribution of organic ligands and mineral binding sites. It is also apparent that although the LCF results indicate an overall mixture of sulfide species, organic associations and iron oxide complexation, the Cu results indicate a lesser role for iron oxides than is apparent in the Zn results. This is in keeping with general literature findings that although Cu and Zn have the capacity to bind with both minerals and organic constituents, Zn has a relatively greater affinity for mineral constituents than is the case for Cu. It is also noted that on plotting the percentage of LCF-derived Fe-ligand species against the Fe content of the biosolids no significant relationship was found.

The μ -XRF elemental maps suggest that despite some evidence that Cu and Zn are sometimes associated with Fe in the sample, this association is not exclusive and a large degree of heterogeneity is present in these materials. Although the Cu and Zn in some areas are associated with large concentrations of Fe (most likely Fe oxides), in other areas this association breaks down.

Numerous studies (e.g. Kukier et al. 2010) showing a persistent long-term decrease in the bioavailability of metals in biosolids amended soils should be recalled. The results of these studies point to the existence of a protection factor in these systems but the mechanisms underlying this effect require further explanation. These mechanisms could relate to the redistribution of metals onto Fe and Mn oxides added with the biosolids upon degradation of the organic matter. Ongoing synchrotron investigations based on differential individual particle analysis (DIPA) in combination with a Na hypochlorite treatment to remove organic matter are focusing on this hypothesis.

ACKNOWLEDGEMENTS

This research was undertaken using the X-ray fluorescence microscopy beamline at the Australian Synchrotron, Victoria, Australia, and the Australian National Beamline Facility BL20-B beamline at the Photon Factory, Tsukuba, Japan.

REFERENCES

- P.H.T., Beckett, R.D., Davis, P., Brindley. 1979. The disposal of sewage sludge onto farmland: The scope of the problems of toxic elements. *Water Pollut. Control.* 78, 419–445.
- G.M., Hettiarachchi, K.G., Scheckel, J.A., Ryan, et al. 2006. μ -XANES and μ -XRF investigations of metal binding mechanisms in biosolids. *J. Env. Qual.* 35, 342-351.
- U., Kukier, R.L., Chaney, J.A., Ryan et al. 2010. Phytoavailability of cadmium in long-term biosolids-amended soils. *J. Env. Qual.* 39: 519-530.

COMPOSITION OF RED MUD VARIES DEPENDING ON SOURCE REFINERIES

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INTRODUCTION

Red mud is a challenging waste problem confronting all aluminium industries. Depending on the source of original bauxite used in the refinery, the composition of red mud has been reported to vary considerably. Understanding the alkalinity, salinity and other associated chemical properties of red mud is of both theoretical and practical importance for red mud treatment and disposal (Carter, Slood et al. 2008). While the composition of red mud has been reported in the literature, most researchers focused on Bayer red mud as Bayer process is the principle refining process being utilized around the world. Approximately 90% of red mud generated every year (around 90 million tons) is derived from Bayer process (Kumar, Kumar et al. 2006). Few cover properties of red mud from sintering process and combined process, which are mainly utilized in China. Therefore, this research examined different red mud samples derived from Bayer process (SDBE), sintering process (SDSJ) and combined refining processes (HNZZ), all of which were collected as bulk samples (20 to 25 kg) from China (CHALCO). Various utilizations including production of building and construction materials, usage as adsorbent or catalysts, making new functional materials are being investigated by most aluminium companies to minimise disposals to landfills.

METHODS

Basic chemical properties

Total element composition of red mud samples were analysed by X-ray fluorescence spectroscopy (XRF). Red mud suspensions (1:5 red mud:water) were prepared to determine the pH, electrical conductivity (EC) and water soluble cations. K, Na, Ca, Mg in the water extract was determined by Inductively Coupled Plasma (ICP).

pH buffering capacity

The pH buffering capacity of red mud samples were determined by slow titration of equilibrated red mud suspension (1g/L) with 0.2 M HCl.

Mineralogical composition

Minerals present in red mud were identified by X-ray diffraction (XRD) which utilized Cu K α radiation at 0.5 °/min scan speed from 10° to 70°. Red mud samples were ground to pass 150 μ m before determination. Poorly ordered oxides (Al, Fe, Si) were determined by acid ammonium oxalate method.

Thermal gravimetric analysis

Thermo gravimetric analysis (TGA) was performed using a TGA 2950 Thermo gravimetric analyser (TA instrument Hi-Res Modulated TGA 2950).

Infrared spectra

KBr pellets of red mud samples were prepared for Fourier transform infrared spectroscopy (FTIR) which was taken in the frequency range 4000–400cm⁻¹ for 256 scans with resolution of 8 cm⁻¹.

RESULTS AND DISCUSSION

Three samples (SDBE, SDSJ, HNZZ) were analysed by XRF, XRD, TGA, FTIR, comparison of their properties is summarized as follow:

- (a) Irrespective of the refining processes used, red mud samples have high pH and salinity;
- (b) Contrary to red mud samples derived from Bayer process (SDBE), samples generated from sintering process and combined process contain less iron oxide and aluminium oxide, but high concentration of calcium oxide due to lime added during refining process;
- (c) Mineral analysis showed that Bayer red mud mainly contains sodalite, hematite, quartz, anatase, calcite, gibbsite, while sintering red mud (SDSJ) is composed of hematite, quartz, (calcite, magenesian), red mud from combined process contains hematite, quartz, calcite, cancrinite, (katoite, silician);
- (d) Different mineral composition of red mud lead to different pH buffering capacity pattern as evident from the titration method;
- (e) FTIR and TGA pattern of red mud confirm the mineralogical composition.

Table 1. Red mud profile and their properties

Sample	SDBE	SDSJ	HNZZ
Origin	Bayer process	Sintering process	Combined process
pH	11.62±0.01	10.81±0.01	11.86±0.02
EC(ms/cm)	4.17±0.05	5.23±0.01	2.83±0.01
Fe ₂ O ₃ (%)	31.48	9.37	6.45
Al ₂ O ₃ (%)	19.57	11.79	21.50
SiO ₂ (%)	24.36	12.66	14.80
CaO (%)	2.35	26.95	26.06
Oxalate extractable Fe (mg/g)	0.35±0.02	46.81±0.23	9.02±0.23
Oxalate extractable Al (mg/g)	48.46±1.15	30.93±0.15	45.88±1.43
Oxalate extractable Si (mg/g)	55.76±1.42	46.50±0.13	35.41±0.91

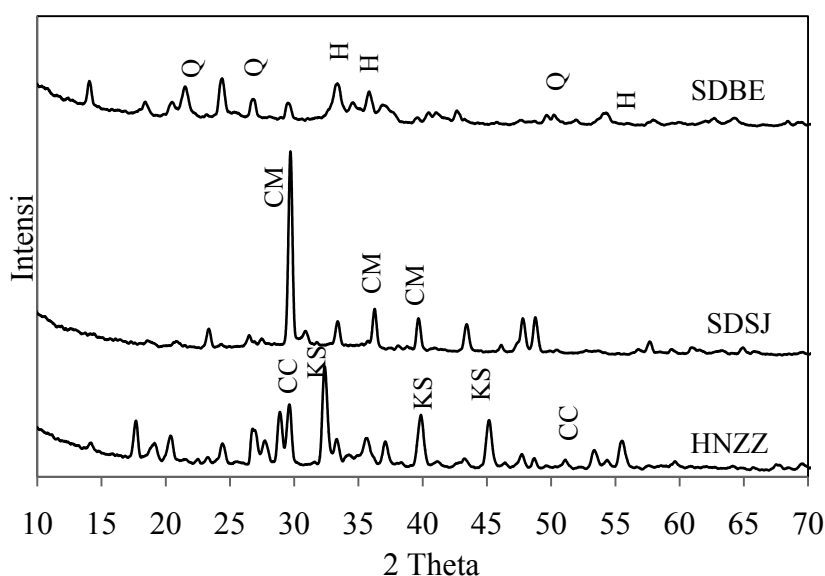


Fig.1. XRD pattern of red mud samples (Q-quartz, CM-(calcite, magnesian), KS-(Katoite, silician), H- hematite, CC-calcite)

CONCLUSIONS

Different minerals are detected in red mud from different refineries, which lead to different pH buffering capacity pattern, and different FTIR, TGA curves.

REFERENCE

- Carter, C. M., H. A. V. d. Slood, et al. (2008). "Characterization of Untreated and Neutralized Bauxite Residue for Improved Waste Management." *Environmental Engineering Science* 25(4): 475-488.
- Kumar, S., R. Kumar, et al. (2006). "Innovative methodologies for the utilisation of wastes from metallurgical and allied industries." *Resources, Conservation and Recycling* 48(4): 301-314.

ENHANCING SOIL CARBON SEQUESTRATION UTILIZING COMPOST

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INTRODUCTION

Application of organic wastes, such as composts, to agricultural land could increase the amount of carbon (C) stored in these soils and contribute significantly to the reduction of greenhouse gas emissions (Lal, 2004). However, one of the problems with the use of organic wastes as a means of C sequestration is their relatively fast rate of degradation, thereby becoming a part source (rather than a full sink) for greenhouse gas emission. Therefore there have been increasing interests in the conversion of compost, manures and other organic residues into biochars in order to reduce the rate of decomposition, thereby enhancing C sequestration in soils (Gunning et al., 2010). However, biochar production is an energy-consuming process and can also lead to the release of greenhouse gases such as carbon monoxide and methane (Gaunt and Lehmann, 2008). Alternative methods can be used to stabilize C in composts and other organic residues without impacting their quality. The objectives of this study include:

- To examine the rate of decomposition of various organic amendments
- To examine the effect of natural clay materials on the stabilization of C in organic amendments

METHODS

Four surface (0-15cm depth) soil samples, one each from different land-use practices (vineyard, vegetable cultivation, arable cropping and sports turf), were used in this study. The organic amendments used in this study include two composts (poultry manure and cow manure composts) and two biochars (poultry manure biochar and green compost biochar). Iron oxide, aluminium oxide and allophane clay were used to examine their effect on the stabilization of organic amendments. The decomposition of organic amendments was measured over a period of 9 months by monitoring the release of carbon-di-oxide using respiration flasks.

The first-order decay rate equation was used to calculate the decomposition rate of C:

$$N = N_0 \exp(-kt) \quad (1)$$

where N_0 is the initial amount of C recovered at day 0, N is the concentration of residual C in the soil at that instant in time and k is the first-order decay rate constant. The C half-life, $t_{1/2}$ being the time taken to reduce C concentration to half of the initial value, was calculated from the rate constant:

$$t_{1/2} = 0.693/k \quad (2)$$

RESULTS AND DISCUSSION

There was a negligible decomposition of biochars and the rate of decomposition of composts was much higher than biochars, with $t_{1/2}$ values ranging from 139 (± 23) days (poultry manure compost) to 9989 (± 1456) days (Greenwaste biochar). It has often been noticed that the rate of decomposition is much higher for manures and composts than biochars which has been attributed to the difference in the nature of carbon in the organic amendments. The physical and chemical structure including surface area, condensation grade and particle size of biochars control their stability in soils (Wardle et al., 2008).

The rate of decomposition of composts was slightly less in vineyard soil than soils from other land use practices. There was no significant effect of soil type on the rate of decomposition of biochars. The vineyard soil contains slightly higher level of Cu than other soils resulting from regular application of Cu fungicides, which may be one of the reasons for the decrease in the decomposition of composts. It has been shown that Cu forms both soluble and insoluble complexes with organic matter, thereby inhibiting the supply of free C for decomposition (Bolan et al., 2011).

The addition of immobilization agents, iron oxide, aluminium oxide and allophone clay decreased the rate of decomposition (Fig. 1). The decrease in the rate of decomposition may be attributed to the difference in the redistribution of C fractions amongst these samples (Fig. 2). The immobilization agents increased the non-labile (1M NaOH) and residual C fractions in the compost amended soils which are less available for decomposition. It has been shown that Fe and Al oxides and allophonic clays immobilize soil C, thereby preventing it from microbial decomposition (Parfitt, 2009).

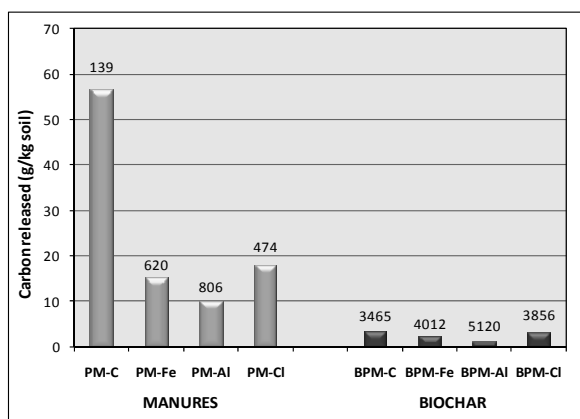


Fig. 1. Decomposition of poultry manure (PM) and biochar (BPM) in the absence (C) and presence of iron oxide (Fe), aluminium oxide (Al) and allophane clay (Cl). The number above the bar indicates the half life ($t_{1/2}$).

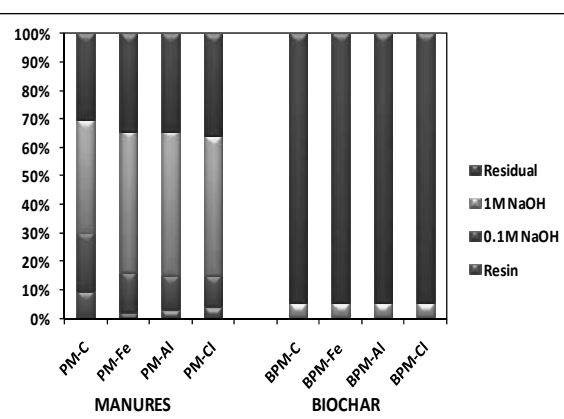


Fig. 2. Distribution of carbon in poultry manure (PM) and biochar (BPM) in the absence (C) and presence of iron oxide (Fe), aluminium oxide (Al) and allophane clay (Cl).

CONCLUSIONS

The long-term storage function of biochars contradicts their fertilizer function that requires a certain biodegradability of the biochar materials. Co-composting of organic amendments with clay materials is effective in the stabilization of C in soil. Stabilization of C in manure composts using clay materials not only maintains their fertilizer value but also would add to the long-term soil carbon pool.

REFERENCES

- Bolan, N.S., Adriano, D., Senesi, N., Kunhikrishnan, A., James, T. and McDowell, R. 2011. Dissolved organic carbon: biogeochemistry, dynamics and agro-environmental significance in soils. *Adv. Agron.* 110:1-75.
- Gaunt, J.L. and Lehmann, J. 2008. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Technol.* 42:4152-4158.
- Gunning, P.J., Hills, C.D. and Carey, P.J. 2010. Accelerated carbonation treatment of industrial wastes. *Waste Manage.* 30:1081-1090.
- Lal, R. 2004. Soil carbon sequestration to mitigate climate change. *Geoderma* 123:1-22.
- Parfitt, R.L. 2009. Allophane and imogolite: role in soil biogeochemical processes. *Clay Miner.* 44:135-155.
- Wardle, D.A., Nilsson, M. and Zackrisson, O. 2008. Fire-derived charcoal causes loss of forest humus. *Science* 320:629

USE OF ORGANIC AMENDMENTS TO IMPROVE THE PROPERTIES OF COAL FLY ASH AS A GROWTH MEDIUM

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INTRODUCTION

Coal-fired power generation is a principal energy source throughout the world. Approximately 70-75% of coal combustion residues are fly ash and its utilization worldwide is only slightly above 30% (Asokan et al. 2005). The bulk of fly ash is deposited in landfills and fly ash basins (Haynes 2009). Establishment of vegetation on these sites serves a number of functions including stabilization of ash against wind and water erosion, reduction in leaching of water and solutes (through water loss as evapotranspiration), provision of shelter and habitat for wildlife and creation of a more aesthetically pleasing landscape. Limitations to revegetation on fly ash can include high pH and attendant deficiencies of Fe, Mn, Cu, Zn, deficiencies of N and P, high soluble salts, toxic levels of elements such as B, natural compaction of fine ash particles inhibiting water infiltration and root growth and a lack of microbial activity and organic matter limiting nutrient turnover (Adriano et al. 1980; Carlson and Adriano 1993; Haynes 2009). Incorporation of various forms of organic wastes (e.g. biosolids, animal manures or composts) into the surface layers of ash could well increase the success of reclamation/revegetation efforts (Haynes 2009). In recent times, incorporation of biochar into soils and mine wastes has attracted interest. Biochar is charcoal material produced as a by-product of pyrolysis of biomass and because of its relatively stable, inert, nature its incorporation is an opportunity to increase C sequestration, thus partially offsetting anthropogenic CO₂ emissions (e.g. from coal combustion) (Lehmann et al. 2006).

METHODS

In this study the effects of addition of three conventional organic amendments (biosolids, poultry manure and green waste compost) with each other and with the addition of a poultry manure-derived biochar on chemical, physical and microbial properties of fly ash was investigated in a laboratory incubation experiment. A subsequent greenhouse study examined the growth of Rhodes grass (*Chloris gayana*) in the treatments.

RESULTS AND DISCUSSION

Addition of all amendments, including biochar, increased concentrations of extractable Mg, K, Na and P and CEC_(pH 7.0). Additions of poultry manure, and particularly biosolids, also greatly increased levels of extractable NH₄⁺ and NO₃⁻-N. Addition of biosolids, green waste compost and biochar resulted in a decrease in macroporosity, a concomitant increase in mesoporosity and, at the high rate of addition, an increase in available water holding capacity. Basal respiration was very low in fly ash and was increased by addition of all amendments; metabolic quotient was markedly greater in control than amended treatments. Biosolids, poultry manure and green waste compost additions all increased microbial biomass C. Rhodes grass is a particularly invasive, vigorous and tolerant species that is commonly used for revegetation of degraded land, waste spoils, and/or contaminated sites in subtropical and tropical environments (Naidu and Harwood 1997). The fact that it survived in the unfertilised control treatments in this experiment, for two harvests, attests to the resilience of this species. Nonetheless, growth of Rhodes grass was extremely low under unfertilized conditions in control, biochar and, to a lesser extent, green waste compost treatments and addition of poultry manure and the lower rate of biosolids resulted in large increases in yields. The depression in yield at the high rate of biosolids addition is likely to be the result of a combination of high soluble salts, and extractable NH₄⁺, NO₃⁻ and P in the

rooting medium. Although biochar additions increased extractable Ca, K, P, Cu, Zn and Mn, CEC, mesoporosity and water holding capacity, they had little or no stimulatory effect on the size of the soil microbial community, N fertility or plant growth. This was attributable to the lack of metabolisable C and an insignificant N-supplying capacity in biochar.

CONCLUSIONS

The higher cost per tonne of a manufactured product such as biochar, compared to conventional organic wastes, will be an important practical concern when considering its use in revegetation. Its use may be warranted where substantial financial and/or public relations benefits accrue from direct C sequestration. Since the lower rate of biosolids and both rates of poultry manure gave the highest yields of grass at both harvests (irrespective of whether a basal fertilizer application was made or not) they could be considered the most successful amendments. Indeed, in order to attain similar yield increases following biochar additions, N would need to be supplied by addition of fertilizer N or organic waste with a narrow C/N ratio. The addition of organic wastes (e.g. biosolids, poultry manure) not only improves soil physical properties and nutrient availability but also increases the size and activity of the soil microbial community; a major advantage when revegetating the biologically inert ash material.

REFERENCES

- Adriano, D. C. and Page, A. L., Elseewi, A. A., Chang, A. C. and Straughan, I. (1980) Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. *J. Environ. Qual.* 9: 333-344.
- Asokan, P., Saxena, M. and Asolekar, S. R. (2005) Coal combustion residues – environmental implications and recycling potentials. *Resour. Conserv. Recy.* 43: 239-262.
- Carlson, C.L. and Adriano, D. C. (1993) Environmental impacts of coal combustion residues. *J. Environ. Qual.* 22: 227-247.
- Haynes, R. J. (2009) Reclamation and revegetation of fly ash disposal sites – Challenges and research needs. *J. Environ. Managem.* 90: 43-53.
- Lehmann, J. (2007) Bioenergy in the black. *Front. Ecol. Environ.* 5: 381-387.
- Naidu, B. P. and Harwood, M. (1997) Opportunities for landscape stabilization and revegetating disturbed lands in stressful environments with exotic and native forages. *Trop. Grassl.* 31:364-369.

EFFECT OF COAL COMBUSTION PRODUCTS ON THE LEACHING OF PHOSPHORUS IN SOILS

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INTRODUCTION

High concentration of phosphorus (P) in soils due to agricultural P (organic and inorganic fertilisers) application poses serious risks to the soil environment and water bodies. The excess P in the soil is prone to movement through the soil profile in the form of either runoff or leaching, because of the lack of sufficient P sorptive mineral (immobile) components like Al, Fe and Ca (McDowell, 2005). The extent of P adsorption is chiefly controlled by the pH, and by the amount of Ca, Fe and Al in the soil solution (Seshadri *et al.*, 2010). Liming of soil not only increases the pH but also the Ca in solution, thereby increasing the P sorption as a result of precipitation as calcium phosphate (Bolan *et al.*, 2003). As an alternative to liming, coal combustion products (CCPs) such as fly ash (FA), fluidised bed combustion ash (FBC) and flue gas desulphurisation (FGD) gypsum are being used for P retention in soil, thereby reducing the P transport to water bodies (McDowell, 2005). The CCPs are generally alkaline with high pH and rich in P sorptive components such as Al, Fe and Ca (McDowell, 2005). Hence, this study will explore the effect of CCPs on P leaching in low P retaining soils, focussing on the effects of pH and concentrations of Ca in solution on P leaching.

METHODS

The leaching experiments were performed using a sandy soil collected from Queensland (Podosol - BIR), which had low P retention capacity (PRC) and pH (Table 1). The CCPs used were FA from Port Augusta power station (South Australia) and FBC from Redbank power station (Queensland), which have been shown to be effective in enhancing P adsorption in soils (Seshadri *et al.*, 2010). The P sources applied to the soils were KH₂PO₄ (PP) and poultry manure (PM).

Table 1. Characteristics of the materials used

Materials used		pH	PRC (%)	Total elemental concentration (mg kg ⁻¹)			
				P	Ca	Fe	Al
Soil	BIR	3.4	4.62	-	169.8	502.6	456.4
CCPs	FA	10.2	-	1522	18040	121300	25170
	FBC	12.7	-	154.3	49680	157600	34020
P sources	PP	-	-	227600	-	-	-
	PM	5.1	-	147800	43510	24890	50500

The leaching of P was studied using column experiments with pulse and step inputs of P, using 60 mL syringe columns (3 cm in diameter and 7.5 cm in height). The soils were thoroughly mixed with the P sources at 100 mg P kg⁻¹ soil (only for pulse input) and incubated with CCPs (at 0 and 15 % w/w application rates) for 21 days at 60 % water holding capacity (WHC). The incubated soils were air dried and 40 g of the dried soils were added in small increments to the columns and packed at a bulk density of 1.18 g cm⁻³. The columns were allowed to saturate with deionised water and then leached with 0.001 mM CaCl₂ solution at a flow rate of 0.74 mL min⁻¹ using a peristaltic pump. For the step-input leaching experiment, the CCPs incubated soil was leached continuously with 100 mg P L⁻¹ KH₂PO₄ solution and the leachates were analysed as explained above. The leachates were collected at definite pore volumes and analysed for inorganic P, pH and concentration of Ca.

RESULTS AND DISCUSSION

In all the leaching experiments, FA showed highest leaching of P followed by the control and FBC. This is attributed to the high P content (Olsen P 260.44 mg kg⁻¹) of FA. Hence, in this research, the leaching of P from FA (amended separately to BIR) was also measured in the absence of P treatment. In order to account for P leaching from FA, the difference between the leachate P from FA with P and FA without P was calculated and plotted in Figure 1. The FBC confirmed the highest P adsorption (Seshadri *et al.*, 2010) as evident from the minimal leaching of P for FBC amended samples. The P leaching in PP treated soils was higher than the PM treated soils, where the P leaching increased gradually, which can be linked to the slow release characteristics of the manure P. The CCPs decreased P leaching (4.18 % for FA and 12.01 % for FBC) in PP treated soil and induced an increase in P leaching (21.46 and 15.33 % for FA and FBC, respectively) in PM treated soil, which is attributed to the mineralisation of PM by CCPs (Seshadri *et al.*, 2010). In the case of step leaching, the CCPs showed effects similar to that of pulse leaching, and P in the leachates appeared faster in the column with no CCPs treatment, followed by FA and FBC (Figure 1 c), indicating the effect of CCPs on P adsorption.

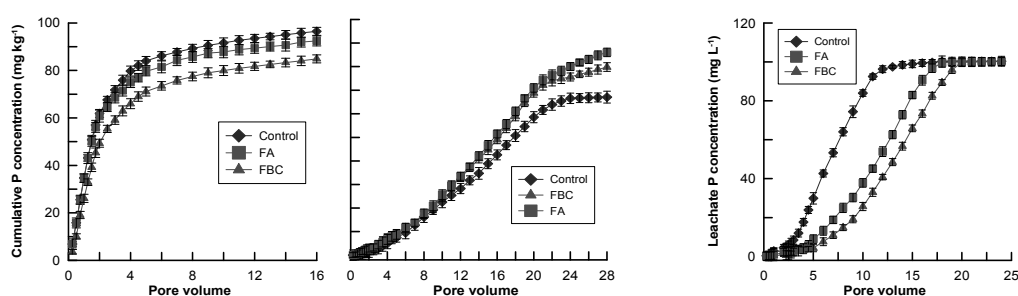


Figure 1. Pulse-input leaching - Cumulative P for soil treated with a. Potassium dihydrogen phosphate (PP) and b. Poultry manure (PM) at 100 mg P kg⁻¹ soil as affected by CCPs (15 % w/w); c. Step input leaching – Breakthrough curves for the soil, treated with PP at 100 mg P L⁻¹ soil as affected by CCPs. Error bars represent the standard deviation between the replicates.

The leachate pH increased consistently for FBC and FA amended samples, whereas control samples showed decreasing trends in the leachate pH. The Ca concentration in the leachates was highest for FA amended samples, followed by FBC. Dou *et al.* (2003) observed that pH and Ca are main factors influencing P solubility in CCPs amended soils.

CONCLUSION

The results clearly indicate that the presence of CCPs decreased P leaching from the sandy soil, with FBC emerging more effective than FA. In the case of PP treatment, the CCPs immobilised the inorganic P thereby reduced P leaching and mobilised the organic P applied as PM, thereby increased P leaching for PM treatment. The increases in pH and Ca concentration in the soil solution significantly influenced the P in the leachates. Hence, CCPs can be used as an effective P sorbent in sandy and poor P retaining soils, thereby mitigating P loss to ground water.

REFERENCES

- Bolan, N.S., Adriano, D. and Curtin, D. (2003). Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Adv. Agron.* **78**: 215-272.
- Dou, Z., Zhang, G.Y., Stout, W.L., Toth, J.D. and Ferguson, J.D. (2003). Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. *J. Environ. Qual.* **32**: 1490-1497.
- McDowell, R.W. (2005). The effectiveness of coal-fly ash to decrease phosphorus loss from grassland soils. *Aust. J. Soil Res.* **43**: 853-860.
- Seshadri, B., Wickremaratne, C., Bolan, N.S., Brodie, K. and Naidu, R. (2010). Sorption and bioavailability of phosphorus in soils as affected by coal combustion products. *In: 19th World Congress of Soil Science.* 1-7 August, 2010. Brisbane, Australia.

A NOVEL TREATMENT OF LIVESTOCK WASTE USING COMBINED UNDERGROUND RIVER DIGESTER WITH UASB SYSTEM

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INTRODUCTION

The rapid development of animal husbandry industries in rural China has resulted in significant environment issues with up to 1 billion ton of forestry and livestock waste generated annually [Wang,1998]. Improper waste disposal pollutes water, air and soil environment. Anaerobic digestion can be used as the primary treatment to reduce livestock waste pollution, at the same time, clean biogas can be acquired. Although the construction cost of the traditional pit digester is low and it is easy to operate, the main disadvantages such as the low gas yield, difficult residue discharge, and limited treatment capacity affect the further development of traditional pit digester. In addition, the residue from anaerobic digester still contains the organic matter, nitrogen, phosphorus and heavy metal that will pollute ecological environment if it is not treated properly before discharge.

In this study, the anaerobic fermentation technology will be combined with mature wastewater treatment technology for treating the livestock waste. The underground river digester will be used as the primary treatment using the fluidized livestock waste as feedstock to achieve continuous biogas production and convenient residue discharge, which will reduce the operating cost [You, et al., 2002]. Then a UASB reactor will be used as the second treatment to further treat the residue from digester and remove the pollutants.

METHODS

An underground river digester is used as the first treatment with 84 m³ effective volume, 15 day retention time for anaerobic digestion and the total treatment capacity of 6.5 m³/d. Livestock waste after 7day digestion will be used as the feedstock of the underground river digester. A 0.4 m underside radius and 6.5 m high UASB reactor will be used as the second treatment with 2.8 m³ effective volume, 12 h retention time, 0.5 m/h rising velocity and 5.6 m³ / d treatment capacity. COD, NH₃-N, gas production rate, gas composition will be detected periodically in order to evaluate the pollutant removal effect and biogas production efficiency from livestock waste by the combined treatment of underground river digester and UASB.

RESULTS AND DISCUSSION

55%-60% COD of livestock waste can be removed after 15d mesophilic fermentation in underground river digester with 30m³/d biogas production. UASB reactor as the secondary treatment can remove 60-70% COD and 70- 80% ammonia nitrogen of the residue wastewater with 5m³/d biogas production. The methane content in biogas can reach 50 to 70%.

CONCLUSIONS

Anaerobic digestion time and load factor are the key factors for the treatment efficiency of the livestock waste. The combined treatment of livestock waste by underground river digester and UASB can effectively reduce the organic material and inorganic compounds such as ammonia nitrogen with clean biogas production, which will decrease the operating cost.

REFERENCES

- Dashan Wang. (1998) Biomass gasification development and renewable energy utilization. *Agricultural Energy*. 6:1-8.
- Jingyuan You, Bo Xiao, Jiakuan Yang. (2002) The orthogonal experiment on anaerobic digestion conditions of municipal solid waste. *New Energy and Technology*.2:28-30.

EFFECTS OF FINE-SCALE SOURCES ON MIXED HYDROCARBON, CHLORINATED AND KETONE VAPOUR BEHAVIOUR

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INTRODUCTION

Petroleum and chlorinated hydrocarbon vapours can pose a threat to human health if they migrate into buildings located on contaminated sites (Davis et al., 2009; Paterson and Davis 2009). Here fine-scale distributions of vapour source concentrations in soil, vapour and major gas concentrations in soil-gas and soil physical properties were determined in a shallow vadose zone to elucidate the relative behaviour of petroleum (benzene, toluene, ethylbenzene and xylene isomers - BTEX), ketone and tetrachloroethene (PCE) vapours.

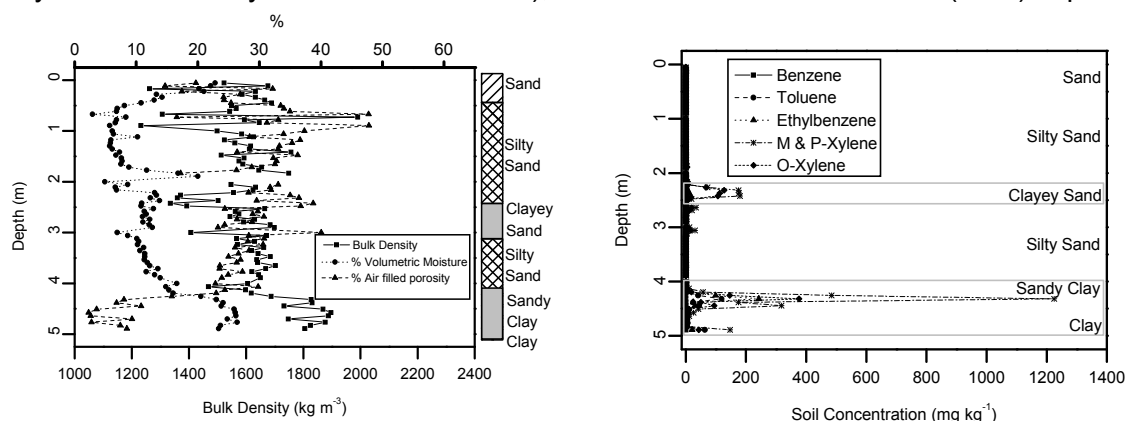


Fig. 1. Depth profiles of (left) soil physical properties and (right) BTEX concentrations in soil.

METHODS

Soil coring used a direct-push technique with a clear polycarbonate liner placed inside a steel sheath with a core retainer on the bottom of the assembly. Five core sections were collected to a total depth of 5 m. The core was described, and sub-sampled at 5 cm intervals for bulk density, percent moisture, air-filled porosity, the fraction of soil organic carbon and volatile organic compounds. Multilevel samplers (MLS) were installed in the same hole as bundles of narrow (3.125 mm) diameter access tubes with sampling ports at 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 m depths. These were sampled for vapour and major gas analyses after purging the dead volume. Analyses were by GC and GC-MS.

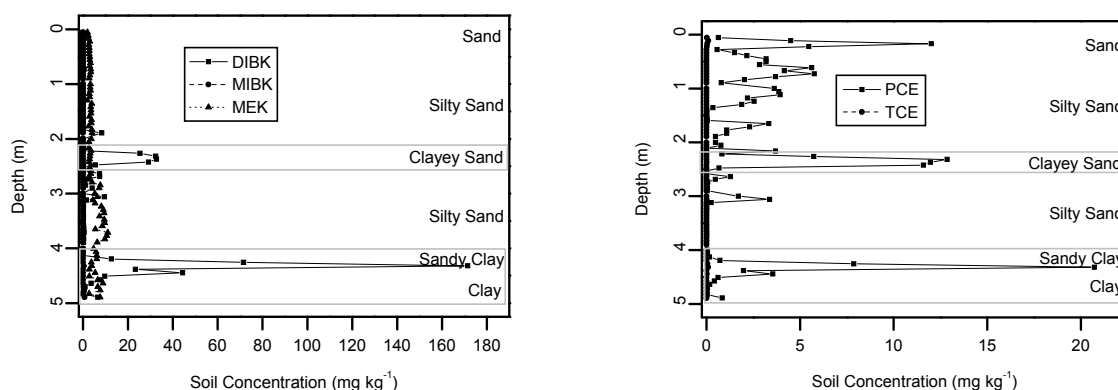


Fig. 2. Depth profiles of (left panel) methylethyl ketone (MEK), methylisobutyl ketone (MIBK), diisobutyl ketone (DIBK) compounds and (right panel) PCE and trichloroethene (TCE) in soil.

RESULTS AND DISCUSSION

Typically, air-filled porosities were quite variable but largely $\geq 0.30 \text{ m}^3$ through the soil profile for depths shallower than 4.25 m (Fig. 1). The soil moisture was typically $> 0.20 \text{ m}^3$ and the air-filled porosity was $< 0.09 \text{ m}^3$ for greater depths, into mainly clay. A discrete horizon with increased clay content occurred at 2.2-2.4 m, and increasing clay content again occurred below a depth of 3.9 m. From analysis of volatile organic compounds in the cores, the peak BTEX (Fig. 1) and DIBK (Fig.2) concentrations were found to coincide with these layers of increasing clay content. Steep concentration gradients over $\leq 0.2 \text{ m}$ were observed. In contrast, PCE (Fig. 2) was distributed more widely over the vertical profile, albeit at much lower concentrations. The data indicate that a mixed non-aqueous phase liquid (NAPL) made up of the BTEX, DIBK and PCE, was located within the layers of increasing clay content. The TPH (Fig. 3) and the MIBK and DIBK vapours (not shown) appeared to be readily biodegraded where oxygen was present – in this case to a depth of $\sim 2 \text{ m}$. PCE vapours (Fig. 3) persisted at shallower depths of the soil profile, but this was also the region of additional PCE sources (Fig. 2), whereas sources of volatile hydrocarbons were restricted to deeper depths. Significant oxygen consumption and carbon dioxide production was also evidence of microbial respiration and potential biodegradation of hydrocarbon and ketone vapours. The relative fluxes of vapours from the thin source areas and partitioning from the NAPL mix requires integration with oxygen ingress and potential biodegradation of the hydrocarbon and ketone compounds to fully assess the flux of vapours and risks in such a profile.

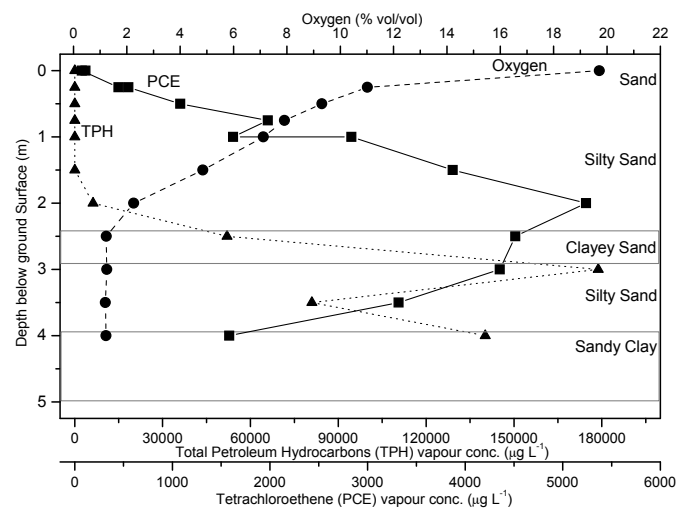


Fig. 3. PCE and total petroleum hydrocarbon (TPH) vapour concentrations and oxygen from sampling soil gas from the MLS.

CONCLUSIONS

Fine-scale clay layering in a soil profile appeared to entrap and act as sources of BTEX and ketone vapours. PCE sources were more widely distributed through the soil profile. This complicates an assessment of vapour attenuation in such a soil profile. Each contaminated horizon remains a potential source of vapours. Such layering may also prove problematic for effective remediation and/or removal of the contaminants.

REFERENCES

- Davis G.B., Patterson B.M. and Trefry, M.G. (2009) Evidence for instantaneous oxygen-limited biodegradation of petroleum hydrocarbon vapours in the subsurface. *Ground Water Monitor. & Remed.* 29(1):126-137.
- Patterson B.M. and Davis G.B. (2009) Quantification of vapour intrusion pathways into a slab-on-ground building under varying environmental conditions. *Environ. Sci. & Technol.* 43(3): 650-656.

ESTABLISHING EXCLUSION CRITERIA FROM EMPIRICAL DATA FOR ASSESSING PETROLEUM HYDROCARBON VAPOUR INTRUSION

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INTRODUCTION

The behaviour of petroleum hydrocarbon vapours in the subsurface has been demonstrated to be influenced by aerobic degradation processes. Aerobic degradation occurs whenever sufficient oxygen is present resulting in the rapid attenuation of hydrocarbon vapours over short distances. Hence aerobic degradation can provide a barrier to vapour intrusion where there is sufficient separation between the source and the building foundation.

The concept of aerobic degradation is considered in the application of the proposed Australian petroleum Health Screening Levels (HSLs). This is based on a modelling approach where it is assumed that hydrocarbons reach the point of exposure, but may then be attenuated (using an adjustment factor where applicable) to account for aerobic degradation. Empirical data from sites in Australia, supported by data from sites in the United States, show that the concept of an exclusion distance can be used as a first step to determine if the vapour migration and intrusion pathway is complete and warrants further assessment.

An exclusion criterion is defined in this study as the thickness of clean soil between a defined source and the ground surface, or slab, over which petroleum hydrocarbon vapours are sufficiently mitigated by natural attenuation to not be considered important with respect to vapour intrusion and inhalation risks. This paper presents the results of an analysis of empirical data that has been compiled from a wide range of petroleum sites in Australia, with comparison against similar data from the United States. The data has been compiled, reviewed and evaluated with the aim of determining if exclusion criteria can be supported for dissolved and non-mobile light non-aqueous phase liquid (LNAPL) petroleum groundwater sources, and adopted in the assessment of vapour risk issues in Australia.

METHODS

A database of paired petroleum hydrocarbon soil vapour and groundwater source concentrations has been compiled over 3 years from sites in Australia, as summarised in Table 1. All data were reviewed in detail to ensure it was suitable for interpretation and interrogation. Hence some data has been excluded from the database due to a lack of source information, problems with data quality and/or conceptual site model issues. This refined database then formed the basis for conducting more detailed reviews that have been focused on establishing exclusion distances.

Table 1. Summary of petroleum hydrocarbon data within Australian database

Information sources	1080 paired soil vapour and groundwater source concentrations from 124 sites Vapour data from single and nested wells, 12% of which are sub-slab
Data reported	Benzene, toluene, ethylbenzene and xylenes (BTEX), volatile total petroleum hydrocarbon fractions (TPH) and hexane (soil vapour only); measurements of oxygen, carbon dioxide and methane in the soil profile; source type and site characteristics
Locations	45% of sites from VIC, 28% from NSW, 10% from SA, 7% from ACT, 4% from QLD, 3% from WA and remaining 3% from TAS and the NT
Sources	Dissolved phase (28% data) and NAPL (72% data) from petrol and/or diesel sources
Soil types	The dominant soil types comprise sand (13%), clay (42%) and sandy clay (45%) 41% of all data sites include groundwater within a fractured rock system

APPROACH AND DISCUSSION

The refined database has been reviewed further to understand:

- the source concentrations that include a range of dissolved phase concentrations and the presence of non-mobile LNAPL;
- depth to the source and soil vapour sampling points;
- indicators of aerobic and anaerobic processes, i.e. levels of oxygen, carbon dioxide and methane in the soil profile;
- presence of a smear zone;
- whether the overlying soil profile can be considered to be clean; and
- concentrations of petroleum vapour in the soil profile, open ground and beneath concrete or building slabs.

To be able to determine vertical distances that may be considered to be exclusion distances the data has been used to determine a separation distance 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. This separation distance has been reviewed in conjunction with the information available on the source, soil type, presence of slabs and supporting data on oxygen and carbon dioxide to determine the conditions under which aerobic degradation can be considered to fully attenuate petroleum hydrocarbon vapours.

These conditions, particularly in relation to source strength, level of oxygen and separation distance have been used to define exclusion criteria.

While some discussion needs to occur before final exclusion criteria can be adopted, the empirical data suggests that the following can be considered in these discussions:

- For low-strength dissolved groundwater sources (benzene < 0.8 to 1 mg/L and TPH < 10 mg/L) - approximately 1.5 to 3m of clean soil between the source and surface or building can be considered sufficient to attenuate hydrocarbon vapours;
- For high-strength dissolved groundwater sources (that do not meet criteria for presence of NAPL) – approximately 3 to 4 m of clean soil between the source and surface or building can be considered sufficient to attenuate hydrocarbon vapours;
- For LNAPL sources and poorly characterised dissolved phase groundwater sources – approximately 10m of clean soil between the source and surface or building can be considered sufficient to attenuate hydrocarbon vapours.

The exclusion criteria determined are relevant to all soil types, including fractured rock systems. It is noted that the definition of clean soil is important to the application of exclusion criteria.

These exclusion criteria are further supported by those derived from data from the United States and, along with some variation in definitions of source concentration and clean soil, are currently being adopted by a number of states, in particular California, New Jersey and Indiana in revisions to petroleum guidance.

The empirical data provide a reality check on the HSLs, with the data generally supporting the HSLs. The use of exclusion criteria provides a straightforward tool that is relevant to all geological types in Australia, for the rapid identification of sites where vapour risk issues will never be of concern, allowing more detailed vapour intrusion/risk assessments to be focused on those sites that have the potential to be of concern.

CONCLUSIONS

Aerobic degradation can provide a barrier to vapour intrusion where there is sufficient separation between the source and the building foundation. This separation distance, along with an understanding of the source strength and soil profile (i.e. presence of clean soil where there is sufficient oxygen for aerobic degradation to occur) has been determined from empirical data collated from Australian sites, and can be supported by empirical data from the United States. The exclusion criteria can be considered as a first stage of a vapour assessment to determine if there is the potential for the vapour pathway to be of significance and if there is the need to conduct a vapour assessment.

VAPOUR INTRUSION MODELLING WITH BIODEGRADATION TO SUPPORT THE ASSESSMENT OF HUMAN HEALTH RISK AT A CONTAMINATED SITE

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INTRODUCTION

Parsons Brinckerhoff (PB) completed vapour intrusion modelling (VI) and human health risk assessment (HHRA) works at a former Bulk Petroleum Depot located in ACT (the site). The objective of the works was to evaluate if concentrations of petroleum hydrocarbons identified in groundwater at the site posed a vapour risk to future users of the site in the context of its development for medium-density residential use (townhouses). The proposed development plan indicated that all townhouses were single storey with slab-on-grade construction.

METHODS

VI models provide an estimation of the chemicals of potential concern (COPC) concentrations in the air due to the migration of volatile hydrocarbons from various sources of contamination, including soil vapour and groundwater, into an enclosed space such as a building or shallow trench.

The widely used Johnson and Ettinger (J&E) algorithm, and associated packages in their base form, assumes a one-dimensional, steady state situation with no biodegradation. However, a review of the recent scientific literature indicates that aerobic biodegradation of petroleum hydrocarbons can, and does occur, and neglecting this process can significantly overestimate human health risk.

VI modelling using the J&E model without biodegradation indicated that the potential for an unacceptable vapour risk could not be excluded. Therefore, PB completed the following to further assess the potential for an unacceptable vapour risk:

- a. Stage 1: review of available models incorporating biodegradation, and selection of an appropriate model.
- b. Stage 2: modelling using the selected model and a 'bare earth' scenario to attempt to verify soil vapour results reported for the site and support the occurrence of biodegradation at the site. Given the oxygen concentration within the geological units of the site was not known, an iterative approach, using different input oxygen concentrations, in the range 6% to 21%, was undertaken.
- c. Stage 3: estimation of the indoor air concentrations inside a residential building with slab on grade construction and concentrations inside a maintenance trench. Stage 3 was completed using the model developed in Stage 1 and considered biodegradation.

The results from Stage 3 were utilised to estimate human health risk using the 'RAGS F' approach.

The COPC were benzene, toluene, ethyl benzene and xylenes (BTEX). Residents (adult and child) and maintenance workers were identified as the populations of concern. The soil profile at the site comprised sandy gravel to approximately 1 m depth underlain by clay, silty clay and sandy clay to between 3 m and 6 m depth, and shale. Groundwater at the site was generally encountered within the shale bedrock between 6.0 and 7.0 m BGL. Both measured groundwater and soil vapour concentrations were considered when determining input COPC concentrations for the VI modelling.

RESULTS AND CONCLUSIONS

From the review undertaken in Stage 1, PB concluded that the Oxygen-Limited VI model packaged as BioVapour (API, 2010) was an appropriate model for use at the site. The results of the Stage 2 VI modelling indicated that the measured soil vapour concentrations could be supported by BioVapor modelling which showed:

- Aerobic degradation is rapid, and occurs in a relatively narrow vertical zone, referred to as the transition layer. In this zone, oxygen and hydrocarbon concentrations do not overlay and are both equal to zero at the interface.
- If 10% oxygen is present in the sand layer across the top 1 m site, this interface will occur 1 m below the sand layer. Measured soil vapour concentrations were reported to be only 0.2% of source soil vapour concentrations at this depth.
- If between 6% and 21% oxygen is present in the sand layer across the site, the interface will range between approximately 0.4 m and 1.8 m depth below the sand layer.

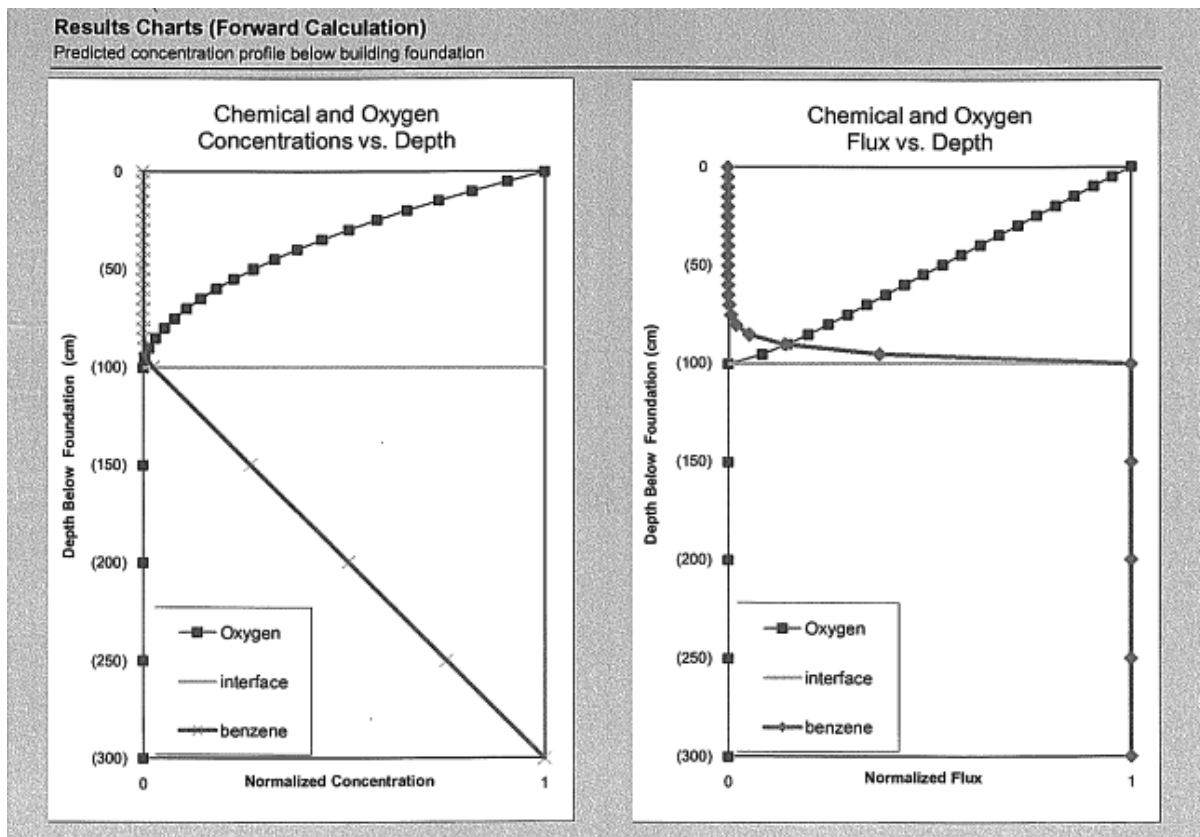


Fig. 1. BioVapour output file assuming 10% oxygen in the sand layer. Note, sand layer not shown.

The Stage 3 modelling and estimation of human health risk demonstrated that the identified COPC concentrations in groundwater were not likely to pose an unacceptable vapour risk to users to future resident and maintenance worker populations at the site in the context of the proposed development.

REFERENCES

American Petroleum Institute (API) (2010) BioVapour User's Manual Version 2.0.

TIME-INTEGRATED vs. GRAB SAMPLING FOR SOIL GAS

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INTRODUCTION

Vapor intrusion (VI) is an exposure pathway of interest for many indoor environments. During the last decade, concern over potential vapor intrusion has led to indoor air evaluations at thousands of buildings in the US and elsewhere to address air toxics such as petroleum hydrocarbons and chlorinated solvents. To help determine the contribution of subsurface sources to indoor air quality, soil-gas samples are routinely collected from immediately beneath building slabs or at depth as part of vapor intrusion studies. The samples often are collected in evacuated, stainless-steel canisters of 6L or 1L volume and analyzed at an off-site analytical laboratory by US EPA Method TO-15.

Existing vapor intrusion guidance in the US typically limits the rate of sampling to 200 mL/min, so compliance with such guidance requires the use of flow controllers to collect a time-integrated sample. Discussions with state regulators in the US suggest that the upper limit on flow rate was set based on professional judgment.

There is a need for empirical data to provide a valid technical basis and justification for any limits on sampling flow rate. Therefore, a field study was undertaken to test whether sampling flow rate had a significant effect on measured concentrations of volatile organic compounds (VOCs) in soil gas.

METHODS

Time-integrated and grab samples were collected at one to two locations at each of four sites to allow a direct comparison to determine whether any persistent bias was introduced by collecting grab samples. At each site, soil-gas samples were collected at a given location both as a time-integrated sample collected at a rate of about 45 mL/min (i.e., 6L samples collected over a two-hour period) and as a grab sample collected over approximately one minute. The grab samples generally were collected immediately after the time-integrated samples over a time period of one minute or less. For the grab samples, the estimated flow rate is in the range of 5,000 to 10,000 mL/min with the canister pressure dropping from about -29 "Hg at the start to about -5 "Hg at the end. All samples were analyzed at certified off-site analytical laboratories using USEPA Method TO-15.

RESULTS AND DISCUSSION

The four field sites are listed in Table 1 along with key information about each site. A sampling depth of 0.2m denotes a sub-slab sample. The location IDs shown here and in the other tables are retained from the original studies for the sake of simplicity, but the specific designations are not intended to have meaning for the average reader.

The soil-gas measurement results are given in Table 2. In general, results are given for each compound detected in both samples above the reporting limit. The results show reasonable agreement between the time-integrated and grab samples. The agreement was best for VOCs detected at relatively high concentrations. For individual data pairs with concentrations $\geq 1,000$ ppbv, the relative percent difference (RPD) is $<15\%$ for eight of nine data pairs. For the compounds detected at relatively low concentrations (i.e., <20 ppbv), greater variability is observed. This variability generally is not significant, however, as the absolute differences in concentration are small and would not influence decisions about the

need for any site mitigation. The typical (pooled) RPD varies from site to site, but is <30% for three of the four sites in the study.

Table 1. Description of Sampling Locations

Site ID / General Location	Location ID	Soil-Gas Sampling Depth (m)	Approximate Depth to Groundwater (m)	Soil Type
A / North Carolina	81s	0.9 – 1.5	10	Saprolite
	85d	6.6 – 7.1	10	Silt & sand
B / Kansas	NW	0.2	5	Fill material
	04	1.5	5	Silty loam & clay
C / Michigan	06	0.2	1.5 – 3	Fill material
D / Illinois	12	3.5	11.6	Clayey sand to sand
	15	6.6	8.1	Clayey sand to sand

Table 2. Comparison of Time-Integrated and Grab Samples

Site / Location ID	Compound	Concentration (ppbv)		RPD (%)	Pooled RPD
		Time-Integrated	Grab		
A / 81s	PCE	15,000	16,000	6.5	Site A = 11.7%
	TCE	25	30	18.2	
A / 85d	PCE	2,400	2,600	8.0	
B / NW	Benzene	6,700	5,800	14.4	Site B = 69.1%
B / 04	Toluene	16	4.4	114	
	m-/p-Xylene	8.0	5.7	33.6	
C / 06	PCE	15	20	28.6	Site C = 28.6%
	TCE	2.1	2.5	17.4	
	Chloroform	4.3	4.2	2.4	
	Chloroethane	3.7	2.2	50.8	
	Freon-12	2.8	3.4	19.4	
D / 12	Hexane	3,200	2,800	13.3	Site D = 17.8%
	Cyclohexane	98,000	100,000	2.0	
	2,2,4-TMP	190,000	170,000	11.1	
D / 15	Benzene	620,000	690,000	10.7	
	Cyclohexane	1,600	1,100	37.0	
	2,2,4-TMP	93,000	84,000	10.2	

The available data set is limited in size but suggests that results for grab versus time-integrated samples are comparable to results for duplicate time-integrated samples. In other words, sampling flow rate does not appear to increase the variability above typical measurement (i.e., sampling + analytical) variability.

The variability of the time-integrated versus grab duplicate samples agrees well with the variability typically seen for conventional time-integrated duplicate samples collected simultaneously using a “T” fitting. The results also are consistent with results reported by other researchers for total hydrocarbons.

CONCLUSIONS

The results indicate that grab samples of soil-gas are equivalent to time-integrated samples and are an acceptable option. The use of grab samples will eliminate the need for flow control devices for soil-gas samples and avoid problems sometimes associated with orifice-type flow controllers (e.g., zero flow due to plugging). The use of grab samples also should result in savings of both time and labor.

VAPOUR INTRUSION INTO SUBURBAN DWELLINGS – WHY VAPOUR DATA ARE IMPORTANT

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INTRODUCTION

In theory, an investigation of site contamination for volatile organic compounds (VOCs) proceeds through a variety of stages, namely a full delineation of the groundwater and soil vapour plume, derivation of a risk estimate, followed by consultation with the community and, generally, as a last step in the data collection process, indoor air testing of residential properties (US EPA, 2002). In practice, environmental reports reviewed by SA Health investigating VOC sites are usually constructed from a limited number of onsite groundwater samples that do not delineate the plume. These data are then modelled to a predicted soil vapour concentration which is then used to derive an often questionable risk estimate – meaningful vapour data are rarely collected. This practice, although it may be cost effective in the short term, is fraught with risk to the community and public health particularly since the models employed by consultants have not been validated for this purpose.

A vapour intrusion case study conducted by SA Health on a vacant residential property impacted by vapour intrusion is presented to illustrate why the collection of vapour data matters for the proper characterisation of this issue from a site assessment perspective.

METHODS

- 1) Several rounds of ambient and indoor air VOC measurements were collected using Radiello® passive samplers (collection time approximately 1 week) in a vacant residential property during autumn and winter of 2010.
- 2) Soil gas monitoring installations were deployed around the building perimeter at a depth of 1 and 2 m and directly under the slab at 1 m. Soil gas samples were collected by Leeder Consulting.
- 3) Vapour flux across uncovered open ground soil and the concrete slab was measured using a vapour flux chamber operated by Leeder Consulting.
- 4) Building and room air exchange rates were measured by FMG Consulting.
- 5) All chemical analysis was provided by Leeder Consulting.

For the purpose of brevity, further details of methods employed in this investigation will be published elsewhere.

RESULTS AND DISCUSSION

As part of routine environmental assessments associated with the decommissioning of a vehicle manufacturing plant, a consultant noted that onsite trichloroethene (TCE) concentrations of > 5 mg/L in groundwater and >60 mg/m³ in soil vapour had been reported for an area adjacent to a number of residential properties. Further investigations by SA Health and the South Australian Environment Protection Authority South Australia identified the following (Evans et al., 2010);

- The boundary of the commercial sites in question did not present a barrier to groundwater or vapour intrusion of TCE, and;
- The results of indoor air testing in the adjacent residential area necessitated the relocation of a number of residents.

A comprehensive vapour intrusion investigation in a vacated residential property from this site, over the autumn to winter period of 2010 presented the following results;

- Ambient air concentrations of TCE varied significantly with soil moisture appearing to play a role.
- Indoor air concentrations of TCE varied over 3 orders of magnitude with preferential pathways demonstrated to contribute substantially to indoor air concentrations (see Figure 1).
- Calculation of indoor air concentrations using vapour flux across concrete and building/room air exchange rates appear to explain observational data only when isolated from the contribution of preferential pathways.

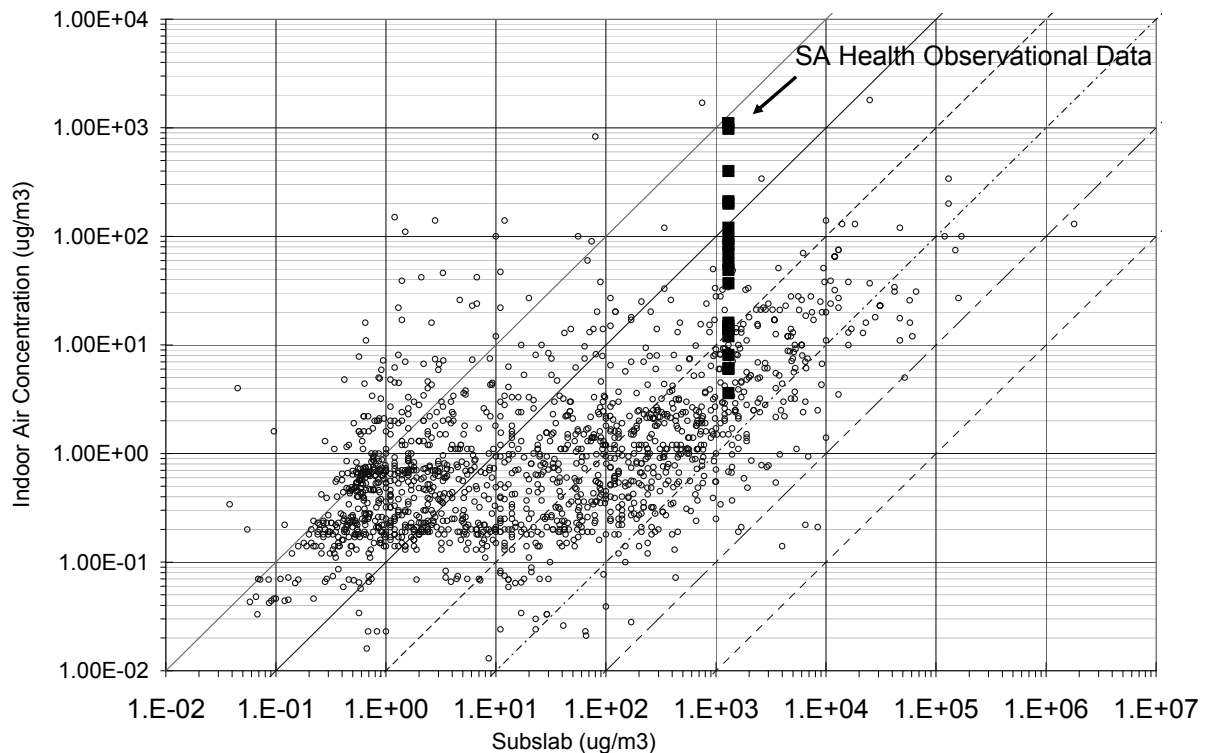


Figure 1. US EPA Draft Vapour Intrusion Database (2008) – a comparison with TCE vapour observations from a vacant residential property at Clovelly Park.

These data demonstrates the need to understand confounding factors at field sites and the importance of direct measurement at residential sites that are by definition complex.

CONCLUSIONS

Observational data presented in this paper indicate that the simplistic ‘point estimate’ calculations of inferred indoor air concentration resulting from vapour intrusion may not reflect the true complexity of the system. A more reliable presentation would be to describe calculated inferred indoor air concentration outputs as a distribution.

REFERENCES

- US Environmental Protection Agency (US EPA). 2002. OSWER draft guidance for evaluating vapour intrusion to indoor air pathway from groundwater and soils (subsurface vapour intrusion guidance). Report No EPA530-D-02-004, US EPA, Washington DC.
- Evans, R., Delaere, I., Babina, K., Simon, D., Nitschke, M. 2010. Vapour intrusion in suburban dwellings. Public Health Bulletin SA, Environmental Toxicology, Vol 7, No 1, pp. 48-52.

COMPARISON OF ACTIVE AND PASSIVE SOIL VAPOUR SAMPLING METHODS FOR SUBSURFACE VAPOUR INTRUSION ASSESSMENT

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INTRODUCTION

Over the past five years a number of regulatory guidance documents and scientific journals relating to vapour intrusion (VI) assessments have been published. Following the release of these documents and information, the focus of regulators and auditors has shifted towards VI assessment data, which is generally gathered in the final stages of contaminated site investigations for human-health based risk assessments. With VI assessments growing in significance within the overall contaminated site investigation process (McAlary 2010), and with new sampling and analysis methods emerging, it is difficult to know what advantages each method offers.

METHODS FOR SUB-SURFACE VAPOUR INTRUSION ASSESSMENTS

VI assessments use soil vapour data which is obtained from various locations and depths within the subsurface of a contaminated site. VI assessment data can be obtained from passive and active sampling methods. Passive sampling involves the use of sorbent media which is left in the subsurface for a known period of time and volatile organic compounds (VOC's) adsorb to the media via diffusive processes. Once retrieved from the subsurface, passive samplers are analysed in the laboratory. Active sampling involves obtaining discrete soil vapour samples from targeted depths by actively drawing the sample out of the formation for collection and analysis. Active soil vapour sampling data is the preferred method for obtaining VI data and USEPA methods TO-15 (canisters) and TO-17 (thermal desorption tubes) are the two most common active sampling methods, (Compendium Method TO-15 and TO-17 1999).

Passive Sampling Methods in Subsurface VI Assessments

There are a number of commercially available, Passive Soil Vapour Samplers on the market and although they work on a similar principal, they use different sorbent media and provide quite different results. Recent technical developments have enabled some passive samplers to quantitate soil gas concentrations. A number of different passive samplers have been used in Australia and they are useful in detecting VOC's in the subsurface at a relatively low cost. The detection limits, desorption processes and analytical suite differs for each passive sampler.

Active Sampling Methods - USEPA TO-15 and TO-17 in Subsurface VI Assessments

Active sampling for VI assessments involves obtaining soil vapour samples from perforated implants which are buried in the vadose zone or beneath a concrete slab and sealed from ambient air pathways. The data (which is presented in $\mu\text{g}/\text{m}^3$) is used in VI models to assess the human health risks associated with residual contamination. Having confidence in the data being used is essential to risk assessors, auditors and regulators when commercial/industrial land is redeveloped for more sensitive land uses.

One of the commonly used active sampling methods in Australia is the USEPA TO-15 method which involves the use of vacuum canisters (Canisters). The canisters come in a range of sizes from <1L to 6L and can be fitted with different flow regulators which

accurately restrict the flow of air into the vessel. Once connected to a sampling point, the valve at the top of the canister is opened and the sample is drawn into the canister under vacuum. The canisters are transported to the laboratory and the sample is analysed via gas chromatography/mass spectrometry (GC/MS), (Compendium Method TO-15 1999).

The other commonly used active sampling method is USEPA TO-17 which uses sorbent tubes to obtain VOC concentrations in soil vapour. A known volume of air (sample) is drawn from the sampling point by a flow calibrated pump and passed through the multi-bed sorbent tubes where VOC's bond to the sampling media. The tubes are then sent to the laboratory and the sample is thermally desorbed from the tubes and analysed via GC/MS, (Compendium Method TO-17 1999).

Comparison of TO-15 and TO-17

Both the TO-15 and TO-17 methods have strengths and weaknesses which have been widely researched and published in scientific journals, (Hayes 2007). Each method has different costs, precision, detection limits and analytical suites and may be better suited to particular site investigations based on a number of considerations including geology, location and contaminants of concern (Hayes 2007 & 2008; McAlary 2010).

Comparison of TO-15, TO-17 and Passive Sampling

Active sampling methods and passive sampling methods offer a range of benefits, some of which are dependent on the purposed use of the data (i.e. VI modelling or site delineation). Each method has proven to have advantages over the others on particular sites, whether it is financial advantages, ease of use or increased accuracy for certain VOC compounds. The detection limits, precision, cost benefit analysis and analytical suites of all three methods have been compared (Hayes 2007 & 2008; McAlary 2010).

CONCLUSIONS

Passive sampling is ideal for site delineation and is an inexpensive and simple tool which can be used to gather site contamination data prior to spending large sums of money investigating soil and groundwater contamination at depth. Recent developments have seen passive samplers used to quantitate soil vapour concentrations. The comparison of TO-15 and TO-17 methods demonstrates that both have positives and negatives and there are many factors to consider when deciding which method to use. Risk assessors, contaminated land consultants, auditors and regulators need to consider this information and make an informed decision about which active sampling method is most appropriate for each particular project.

REFERENCES

1. Compendium Method TO-15 (1999) The Determination of Volatile Organic Compounds (VOC's) in Air Collected in Specially-Prepared Canisters and Analysed by Gas Chromatography/Mass Spectrometry. Center for Environmental Research Information Office of Research and development U.S. Environmental Protection Agency, Cincinnati.
2. Compendium Method TO-17 (1999) Determination of Volatile Organic Compounds in Ambient Air using Active Sampling Onto Sorbent Tubes. Center for Environmental Research Information Office of Research and development U.S. Environmental Protection Agency, Cincinnati.
3. Hayes, HC, Mahfood, J, Shamory, B (2008) Comparison of EPA Compendium Methods TO-15 and TO-17 for the Measurement of Naphthalene in Soil Gas, Business of Brownfields, Pittsburgh.
4. Hayes, HC (2007) Evaluation of Sorbent Methodologies for Hydrocarbon Impacted Site Investigations. A&WMA Vapour Intrusion 2007, September 2007.
5. McAlary, T & Davis, G (2010) Vapour Intrusion – International Perspectives and Lessons Learned, ACLCA Short course, August 2010.

DETERMINING THE MOST APPROPRIATE SAMPLING TECHNIQUE FOR ASSESSMENT OF VOLATILE CONTAMINANT EXPOSURE

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INTRODUCTION

When assessing the potential risks resulting from exposure to volatile contaminants the most common method is to estimate indoor and outdoor air concentrations from contaminated soil and groundwater. Vapour models generally used to estimate these concentrations quite often result in an overestimation of the likely air concentrations. Therefore the most appropriate data for estimation of chemical concentrations in air is analytical data from direct soil vapour, surface emission or ambient air samples. The increased accuracy provided through the use of direct sample analytical data is therefore becoming increasingly popular with regulators and governing bodies.

SITE SPECIFIC CONSIDERATIONS

A number of different site specific features will need to be considered when choosing the most appropriate vapour sampling techniques. These may include:

- The nature of volatile contaminants present.
- Depth to groundwater/capillary fringe.
- Depth to soil contamination.
- Details of future developments that may take place at the Site.
- The geological profile of the Site.

SAMPLING TECHNIQUES

A number of different methods are available for collection of air samples. However, determination of the most appropriate method for sampling can often be difficult and must be assessed on a site by site basis.

This paper will discuss the advantages and disadvantages of the techniques available for soil vapour, surface emission and ambient air sampling; and the variability of sampling conditions that can occur and the range of analytical options available for analysis of air samples.

Soil Vapour Sampling Methods – Site specific soil vapour data can provide information on volatile contaminant concentrations beneath buildings, pavements and open areas, thus providing information on partitioning and attenuation that may not be addressed or may be over/underestimated by models. Soil vapour sampling can be undertaken from permanent or temporary probes and thus can be used at a range of contaminated sites. It is also possible to detect low concentrations of compound such as benzene, naphthalene and vinyl chloride. This data can be used directly in exposure models to estimate the migration to and across the surface into indoor or outdoor air.

Surface Emissions – Sampling of surface emissions can provide a direct measure of emission into ambient air and thus eliminate the need for sub-surface vapour migration modelling. There are a number of external factors that can influence results of this form of sampling and the process of sampling surface emissions has a range of advantages and disadvantages.

Ambient Air – This method of sampling can provide a direct estimate of the concentrations likely to be encountered in the breathing zone at the site. However, sampling of ambient air concentrations can result in detection of contaminants from a range of sources and can thus

make it hard to determine the actual risks posed to the receptor from site related contamination. Reported concentrations can be subjected to a high level of variability as a result of ambient weather conditions and building ventilation (e.g. open or closed doors and windows, air conditioning/heating). An accurate estimate of breathing zone exposures may require numerous sampling rounds to ensure that results are representative.

A common sampling technique used to collect soil vapour, surface emission and ambient air is sampling using summa canisters (Figure 1). This method of sampling enables collection of a whole air sample that will provide directly comparable exposure data. Summa canisters also do not rely on adsorption of chemical contaminants and thus there is no potential that chemical breakthrough will occur resulting in an underestimate of chemical concentrations. The choice of technique may be critical in enabling a more accurate assessment of the risk posed to receptors at contaminated sites and those who occupy adjacent properties. Therefore a thorough understanding of the range of techniques available and the advantages and disadvantages of each are essential.



Figure 1: Soil vapour sampling using summa canisters.

ANALYSIS

There are a number of analytical techniques which can be used to quantify the concentrations of volatile samples. These include for active samples: US EPA TO-15 (Summa canisters), US EPA TO-17 (thermal desorption tubes), Charcoal (solvent extraction), Polyurethane foam (PUF)/(XAD-2) less volatile compounds. Analytical passive techniques include: SKC, 3M, Radiello and Gore sorbers.

CONCLUSIONS

There are a number of variables to consider when selecting the most appropriate vapour sampling technique in order to quantify potential risks to human health from a given site. There is no “one size fits all” with respect to the site, development, sampling technique and analytical methods employed when quantifying vapour emission data. AECOM have summarised a number of approaches with key considerations on which techniques are more suited to what conditions.

REFERENCES

USEPA TO-15-Determination of Volatile Organic Compounds in Air, Collected in Specially Prepared Canisters and analysed by GC/MS. January 1999.
USEPA TO-17-Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, January 1999.

EVIDENCE BASED REMEDIATION DECISION-MAKING FOR VAPOUR INTRUSION RISK FROM PETROLEUM HYDROCARBONS

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INTRODUCTION

Vapour intrusion has become a common risk driver in petroleum-contaminated site decision making. Until recently, the methods available for assessing vapour intrusion risk have output extremely conservative results, and this has caused unnecessary expenditure of time and money on lengthy assessments of sites where the actual risk of vapour intrusion was likely to have been extremely low. The publication of CRC CARE'S draft Health Screening Levels (Friebel & Nadebaum 2010) together with guidance on biodegradation of petroleum hydrocarbons (Davis et al 2009) offers a much improved assessment process. However, there is still a significant gap in guidance around remediation decision making. This paper examines some recent developments in international guidance and suggests some approaches for tackling situations which are poorly covered by the guidance.

SCREENING SITES FOR VAPOUR INTRUSION RISK

The historic difficulty with modelling petroleum hydrocarbons stems from the adoption of the USEPA's model for predicting soil vapour concentrations from soil and groundwater, which does not include consideration of biodegradation. Evidence from many sources shows that when oxygen is available, petroleum derived vapours will biodegrade rapidly (eg, DeVaul 2007). Davis et al (2009) suggest that given 5% oxygen in soils, and a limited hard cover slab dimension, it is reasonable to assume biodegradation generically. They offer factors to be applied to vapour measurements at depth to provide a conservative prediction of vapour concentrations potentially reaching the receptor building. This approach was adopted in the guidance supporting the HSLs, permitting the calculation of biodegradation-inclusive screening criteria. As a result of this development, use of the HSLs will be effective in screening out vapour intrusion risk at a reasonably early stage on sites where the source is deep and receptor buildings are in existence.

Analysis of soil, groundwater and soil vapour datasets (Davis, 2010; Wright 2010) provides an alternative possible approach to screening based on empirical evidence. This approach has recently been proposed by the State of California (California SWCRB 2010). The data indicate that across a significant dataset in the US and Australia, whether petroleum vapours will biodegrade can be predicted by the source concentration and the depth of clean soil overlying the source. The datasets include a proportion of measurements made beneath slabs and with phase separated hydrocarbons present. California SWRCB (2010) proposes screening criteria based on the above research including a distance of 5ft clean soil for soil sources (concentration independent) and low-concentration groundwater sources.

REMEDICATION DECISION-MAKING

The screening mechanisms above are likely to be successful in removing sites from further consideration where vapour intrusion risks are negligible. For sites where a risk may be present, the process for determining whether remediation is required is much less clear, especially when the receptor building does not yet exist.

Potential approaches to generating practical remediation criteria include:

- (a) Site specific modelling can be used to generate clean-up criteria. Use of site specific soils parameters, petroleum product compositions, building characteristics and source dimensions can be effective in generating less conservative criteria than the HSLs. This is a useful approach for groundwaters, however the soil criteria generated are still very low, and likely to be below practical remediation levels. Unless biodegradation can be relied upon, site specific modelling will not be effective in limiting the depth to which soil remediation will be required. This means that for a future development, it may be effectively impossible to derive a practical model-based soil clean-up level.
- (b) Site specific modelling can be used to generate soil vapour criteria. This approach results in practical clean-up levels, however validation is more complex than normal since a soil vapour sampling validation programme would be needed. For deep sources this would be practical for unspecified future buildings, however for shallow sources simulating a large slab in the field is costly. Vapour based validation also has the disadvantage that there may be some time between completing remediation and successfully validating the site, which is impractical in many circumstances.
- (c) The concept of distance exclusion criteria could be used to specify a depth-based remediation. For example, if a remediation creates 2.5 m of clean soil above a source, the Davis (2010) dataset can be used to demonstrate no risk of vapour intrusion even if this cannot be proven by modelling. The dataset includes data from a range of circumstances including large slabs, and provides empirical evidence that a thickness of clean soil to provide reliable attenuation can be specified, even where a large slab is present. The method therefore should be applicable for unspecified future buildings, provided that they are within the range of circumstances covered by the dataset. It is not likely to work where PSH is present. Future publication of the dataset analyses in peer reviewed journals will greatly enhance the usefulness of the work, particularly with provision of more detailed information on the situations which the data represents.
- (d) Under some circumstances it may be more cost-effective to install precautionary vapour intrusion mitigation measures in buildings than it is to attempt a remediation that will provide adequate confidence that the risk is sufficiently managed.

REFERENCES

- California State Water Resources Control Board (2010) *Leaking Underground Fuel Tank Guidance Manual – Draft for Public Comment. Version 2.0 October 4 2010*
- Davis, G.B., Patterson, B.M. and Trefry, M.G (2009). *Biodegradation of petroleum hydrocarbon vapours* Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia
- Davis, R. V. (2010) *Evaluating the Vapor Intrusion Pathway: Studies of Natural Attenuation of Subsurface Petroleum Hydrocarbons and Recommended Screening Criteria*, Annual National Tanks Conference and Exposition, New England Interstate Water Pollution Control Commission (NEIWPC), Boston, Mass, Sept 2010
- Friebel, E. and Nadebaum, P. (2010) *Health Screening Levels for petroleum hydrocarbons in soil and groundwater. Part 1: Technical development document (DRAFT)* Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia
- Wright, J. (2010) *Review of Petroleum Vapour Data from Australia*, Ecoforum2010 paper 039, 23-24 February 2010, Australian Technology Park, Sydney

COMPARISON OF TECHNOLOGIES FOR ASSESSING VAPOUR INTRUSION IN FUTURE STRUCTURES FROM SUBSURFACE SOURCES - CASE STUDY WITH SIDE-BY-SIDE MEASURED FLUX AND J&E MODELLING

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INTRODUCTION

A field study was conducted in order to assess the efficacy of using direct flux chamber measurements and soil gas sampling/modelling to assess potential vapour infiltration into future buildings on a development site underlain with compounds found in groundwater. This is a rare opportunity to compare the utility of these preferred technologies for the application of assessing potential exposure to vapours from subsurface groundwater contamination. There are three basic approaches for assessing vapour infiltration into buildings: soil gas or groundwater testing and vapour transport modelling, measurement of compounds found in indoor air compared to outdoor air, and direct flux chamber measurements on the land surface using the US Environmental Protection Agency (USEPA) flux chamber assessment technology. Without any structures or buildings on site, the assessment technologies are limited to soil gas and/or groundwater testing and vapour transport modelling, and direct measurement of VOC flux at the land surface.

METHODS

A field study was designed and implemented where a parcel in the development area was tested at multiple locations using soil gas sampling and direct flux chamber measurement at the same locations. Soil gas data were used in the Johnson and Ettinger (J&E) vapour transport model (J&E 1991 and USEPA, 2002) to estimate the flux of study compounds at the surface in order to allow for a comparison of assessment technologies. In addition, soil parameter data (coring and sampling) were also collected as input to site-specific modelling. The comparison study included the collection of samples using (1) validated USEPA surface emissions isolation flux chamber assessment technology (dynamic flux chamber, USEPA, 1986a and 1986b), (2) regulatory approved soil gas sampling and analysis (USEPA, 1997 and CA EPA, 2004), and (3) soil boring and soil properties testing. The proposed comparison study included side-by-side testing using these two gas-phase assessment technologies at two of the four study stations; the soil properties testing supports the modelling and data evaluation aspect of the comparisons study.

This study area was selected to represent an area of interest with relatively uniform groundwater plume concentration and known lithology. The depth to groundwater in the study area was approximately 60 feet.

The assessment of VOCs from open soil for site assessment purposes is well documented, and the recommended and commonly used direct flux measurement technology is the USEPA (1986a and 1986b) dynamic flux chamber with sample collection and analysis by USEPA (1997) Method TO-15 using both full scan analysis and selective ion mode (SIM) analysis. Soil gas was collected at low depths (5' bgs and 10' bgs) using a sample collection

approach as described in the USEPA and California Environmental Protection Agency (CA EPA), Department of Toxic Substances Control (DTSC) User's Guide (CA EPA, 2004) for soil gas sampling and analysis. Vapour transport modelling was conducted using the J&E, (1991) equation.

RESULTS AND DISCUSSION

These results show that the modelled flux for chloroform, benzene, and 2-butanone using soil gas data are consistently higher as compared to the measured surface flux. The modelled flux values are on the average 15, 13, and 13 times higher than the measured surface flux values for chloroform, benzene, and 2-butanone, respectively.

In addition, the J&E (1991) model was used to estimate surface flux from two groundwater wells with the water table depth at 60' bgs. This comparison of surface flux estimates demonstrates the conservative estimate of surface flux using transport modelling and groundwater data (60' bgs) compared to soil gas/predictive modelling (5' and 10' bgs) and measured surface flux. The modelled estimate using groundwater data is 1,300 times higher than the soil gas/predictive model estimate and about 11,000 times higher than the measured surface flux estimate.

CONCLUSIONS

The comparison of predictive surface flux values using groundwater concentration data in a predictive model and soil gas data in a predictive model show the progression from screening-level estimate to quantitative measurement of surface flux. As would be expected, the uncertainty/conservativeness decreases as advanced techniques are used.

The comparison of surface flux data to soil gas data illustrates the utility of these source assessment technologies. The methods that rely on transport modelling, the soil gas/groundwater sampling and transport modelling approach are more conservative than the direct flux measurement. The results further document the conservativeness of the diffusive transport modelling component of the J&E (1991) model used to estimate transport of vapours from the sub-surface to indoor air.

REFERENCES

- US Environmental Protection Agency (USEPA). (1986a) *Air Superfund National Technical Guidance Study Series, Volume 2: Estimation of Baseline Air Emissions at Superfund Sites*", Interim Final, EPA-450/1-89/002, Office of Air Quality Planning and Standards,.
- US Environmental Protection Agency (USEPA). (1986b) *Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber- User's Guide*. EPA 600/8-86-008 (NTIS PB86-223161), February.
- US Environmental Protection Agency (USEPA), (1997) *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd Ed. Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Collected in Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography/Mass Spectrometry*. Center for Environmental Research Information, Office of Research and Development, January.
- US Environmental Protection Agency (USEPA). (2002) *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*. November.
- California Environmental Protection Agency (CA EPA). (2004) *Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air*. Interim Final. California Environmental Protection Agency, Department of Toxic Substances Control. December 15.
- Johnson, P.C., and Ettinger, R.A. (1991) Heuristic Model for Predicting the Intrusion Rate of Contaminated Vapors Into Buildings. *Environmental Science and Technology*, #25, 1445-1452.

THE IMPORTANCE OF APPLYING STRICT QA/QC PROCEDURES IN THE FIELD AND IN THE LAB TO PRODUCE PASSIVE SOIL GAS DATA THAT WILL SIMULTANEOUSLY IDENTIFY HOT SPOTS AND DELINEATE TRACE CONCENTRATIONS IN GROUNDWATER

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INTRODUCTION

To accurately design a conceptual site model (CSM) and streamline your remediation and monitoring program, you must begin with accurate data. Passive soil gas (PSG) surveys are a versatile technology that have been demonstrated to cost-effectively guide projects where volatile and semi-volatile organic compounds (VOCs and SVOCs) are of concern. A well-designed PSG survey will minimize data gaps to overcome spatial variability challenges and better define source areas and vapour intrusion pathways, as well as delineate the lateral extent of contamination in the vadose zone. However, certain QA/QC procedures must be followed to obtain data that is of known quality and defensible.

METHODS

Advanced PSG methods utilize state-of-the-art hydrophobic sorbents that are in contact with soil vapour for a period of several days to several weeks depending on the project objectives and site geology to passively trap organic compounds present in the soil vapour. PSG samplers are typically installed in approximately 25 mm diameter holes advanced to a typical depth of 30 to 90 cm or by use of suspending the sorbents beneath surface placed, non-intrusive stainless steel flux chambers. The ability to simultaneously collect time-integrated samples in a grid-pattern placement allows for a high-resolution assessment of the spatial variability of contaminants over a wide-range of geologic conditions. Using a traditional site investigation approach of collecting only soil and groundwater data, results in an inadequate delineation of the contaminant distribution from the project start. This limited site investigation approach often results in an incomplete or misleading conceptual site model, an inaccurate risk evaluation, and a failed remediation effort.

Application

The use of 74 PSG samples in a mature urban environment allowed for the identification of source areas and the delineation of the resulting tetrachloroethene (PCE) plume that had impacted a groundwater well. Established QA/QC procedures in the design of the sampler and analysis of the samples were followed to ensure data was not only of known quality and defensible, but also that the survey results were able to identify source areas with PCE concentrations in groundwater at 17,000 ppb while still delineating the PCE plume in groundwater with concentrations as low as 6.8 ppb.

RESULTS AND DISCUSSION

The subject project included sampling near suspected source areas of PCE, including drycleaners and industrial facilities that were identified during the Phase I investigation to have used or potentially used PCE. PSG samples were collected on private properties, as well as along public right-of-ways between the impacted groundwater well and the suspected properties. Following the PSG survey, 11 groundwater samples were collected to correlate with the passive soil gas data. The groundwater samples confirmed the results of the passive soil gas survey, which had identified the source areas and the approximately 800 meter long PCE plume. The PSG sampler design and the robust analytical method

developed allows for a very low reporting limit while still being able to report data that are more than three orders of magnitude greater than the reporting limit.

CONCLUSIONS

When groundwater is impacted with organic contaminants, such as PCE, the cost to identify the source areas and plume migration pathways can be very high, with the cost increasing with the number of soil and groundwater samples that are required for investigation. PSG surveys allow for a cost effective approach to provide a better understanding of the nature and extent of the impacts and allow a focused subsurface investigation, which subsequently reduces drilling and overall sampling costs. When established QA/QC procedures are followed both in the field and in the laboratory, resulting PSG data will best reflect the actual subsurface concentrations which can be confirmed with a limited number of soil and/or groundwater samples.

REFERENCES

Clarke, J., Goodwin, D., O'Neill, H. and Odenchantz, J. (2008) Application of Passive Soil Gas Technology to Determine the Source and Extent of a PCE Groundwater Plume in an Urban Environment, *The Journal of REMEDIATION*, Wiley Periodicals, Inc., Vol. 18, No. 4, pp. 55-62.

INTERLABORATORY COMPARISON OF ANALYSIS OF VOLATILES (INCLUDING BTEX) IN AIR SAMPLES

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INTRODUCTION

The demand for accurate measurement of volatile organic compounds (VOCs) in air samples has risen dramatically recently. This technique consists of collecting an air sample into a passivated stainless steel canister, using a regulated flow device, followed by laboratory analysis using Gas Chromatograph – Mass Spectrometer (GC-MS). The analytical method is based on the established US EPA TO15 method which has been routinely used overseas for some time, and has become increasingly popular in Australia, where it is applied to measurement of VOCs in ambient air, vapour intrusion, and soil vapour from contaminated sites. The VOCs reported by this technique range from C3 to C12, covering halogenated and oxygenated compounds. BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) are an important subset of VOCs, due to the toxicity attributed to benzene (IARC Monographs). Chemical standards used to quantify target analytes are sourced either as liquids or gases to be combined, or as 'ready made' mixtures. Currently there is no easily accessible proficiency study program for laboratories to assess their performance to ensure the highest quality measurements. This study compared the commercially available 'ready made' gas standards with mixtures made up from liquid and gas standards at three different analytical laboratories. This study was not a formal proficiency testing program, but was undertaken as part of quality improvement.

METHODS

National Measurement Institute Standards and Methods

Calibration standards were prepared by adding purified water to a certified clean canister, followed by an aliquot of 1 ppmv commercial gas standard then zero air using an automated standard dilution system. The calibration curves are established for 64 VOCs for the range 0.5 – 50 ppbv in air. After use all canisters and sampling flow devices are cleaned by automated cycles of filling and evacuating with humidified nitrogen. Canisters are certified clean after undergoing analysis and passing certification requirements.

The NMI analysis method for air samples collected into canisters involves pressurising canisters to 10 psig (gauge pressure) with zero air using an automated sample dilution system, a dilution factor is applied to analytical results. A known volume of the mixture is passed through a cooled (25°C) multi-bed sorbent trap. The trap is dry purged with helium to remove water, then the trap is heated rapidly (40°C/sec to 320°C) and the analytes transferred to the Gas Chromatograph with helium. The target compound ions are acquired by a Mass Spectrometer they elute from the GC column using SIM/SCAN mode, which also allows for library search matching of non target compounds.

Queensland Health Standards and Methods

The Queensland Health comparison standard (QLD1) was prepared by spiking a Tenax sorbent tube with 4 µL of a BTEX (125 ng/µL) in methanol standard. The tube was heated to 250°C and the analytes desorbed into a clean evacuated 6 L canister. The canister was pressurised to 24.87 psig with zero air. The theoretical concentration of each compound is given in Table 1. A blank (QLDBLK) canister was prepared by the same method without

spiking the standard onto the sorbent tube. The Queensland Health analysis method is also based on the thermal desorption/GC-MS technique, using multi-stage sample capture/water removal. Calibration standards are prepared by diluting commercial gas standards in a similar manner to NMI.

R J Hills Standards and Methods

The R J Hills standard (NZ1) was prepared by combining aliquots of 1 ppmv commercial gas standards (from a different supplier to NMI) into a clean evacuated 6 L canister. Gas tight syringes were pre-rinsed with the standards then used to transfer aliquots to certified clean canisters via Micro-QT2™ valves. Purified water was added and the canister filled to 15 psig with zero air. A blank canister (NZBLK) was prepared by the same method using only purified water and zero air. The R J Hills analysis method involved concentrating 125 mL of sample, followed by GC-MS analysis. Quantification was performed by extracting ions from the total ion current.

RESULTS AND DISCUSSION

The BTEX results from the analysis of the comparison standards are shown below, the theoretical or target concentration of the interlab sample is given, along with the analytical result from each laboratory. The interlab % RPD was calculated by the absolute difference of the two analytical results divided by the mean.

Table 1. Comparison of standard prepared by QLD Health.

QLD1	Theoretical value (ppbv)	NMI Result (ppbv)	QLD Health Result (ppbv)	Interlab %RPD
Benzene	9.7	8.9	10.0	11.6
Toluene	8.2	9.1	7.9	14.1
Ethylbenzene	7.1	7.5	7.2	4.1
m, p-Xylene	7.1	7.9	7.7	2.6
o-Xylene	7.1	7.1	6.7	5.8

Table 2. Comparison of standard prepared by R J Hills.

NZ1	Theoretical value (ppbv)	NMI Result (ppbv)	R J Hills Result (ppbv)	Interlab %RPD
Benzene	8.2	8.3	9.1	8.6
Toluene	8.2	7.7	7.9	2.3
Ethylbenzene	8.2	8.2	7.4	10.8
m, p-Xylene	16.4	15	14.5	3.2
o-Xylene	8.28	7.8	7.8	0

CONCLUSIONS

The comparison indicated acceptable variation (<20% RPD) between laboratories, with similar differences between measured and target concentrations of the interlab standards. For several of the less volatile TO15 compounds, a systematic difference was seen for one of the preparation methods, which has since been overcome by heating all parts of the dilution process. A formal proficiency program using real air samples will provide assurance to the end users of the analytical results that the correct result has been reported for real samples, and assist laboratories in improving their methodology.

REFERENCES

- Compendium Method TO-15: Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). U.S. Environmental Protection Agency, 1999
 IARC Monographs, 29, 93-148, 391-398, 1982

VAPOUR INTRUSION RISK EVALUATED BY MULTIPLE LINES OF EVIDENCE – A TCE CASE STUDY

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INTRODUCTION

In recent times technical guidance on approaches to evaluate human health risks from the intrusion of toxic soil vapours into indoor air has come from the National Environment Protection Measure (NEPM) (1) process and from CRC CARE (2). These and other guidance documents discuss how measured data on soil vapour and groundwater may be used as input parameters to vapour intrusion (VI) models; discuss the use of surface flux and ambient air measurements and consider the use of empirically derived soil to indoor air attenuation factors. The approach generally adopted in VI risk investigations is to initially use a predictive model in a screening mode using soil or groundwater contaminant data as input data, and if the model predicts an unacceptable risk, measured soil vapour or sub-slab data are used as 'down-stream' inputs to further model runs. In this study, measurements were taken at several points along the VI exposure pathway – groundwater, deep and shallow soil vapour, sub-slab vapour, surface mass flux and indoor/outdoor air concentrations and comparison made to model predictions. The soil vapour to indoor air attenuation factor was also used to compare with other predictions of VI risk.

METHODS

The numerical model used was the US EPA spreadsheet implementation of the Johnson and Ettinger 1991 vapour intrusion model (J&E model). Soil vapour concentrations in boreholes adjacent to a building foundation slab were measured at nested depths of 1, 2, 3 and 4 m below the surface. Sub-slab vapour concentrations were measured by penetrating the concrete flooring at three locations. Samples were collected and analysed using the TO-17 method (active sampling onto sorbent tubes). Mass flux from the concrete warehouse floor was measured using both passive and dynamic flux chambers (Heggie & Stavropoulos) (3). Ambient indoor and outdoor air was measured using Radiello (4) passive samplers.

RESULTS AND DISCUSSION

Using a measured TCE concentration in groundwater of 380 µg/L, at 5.5 m depth, the model predicted an indoor air concentration of 8.4 µg/m³. Based on the water to air partitioning, the Henry's law coefficient, the predicted concentration of soil vapour immediately above the saturated zone was 122,000 µg/m³, somewhat less than the measured soil vapour concentrations higher in the profile, where the maximum concentration of 530,000 µg/m³ was measured at a depth of 3 m. It was thus considered probable that a soil source, rather than a groundwater source was driving the vapour intrusion risk.

Using the model to predict indoor air concentrations from the deepest soil vapour measurement, 450,000 µg/m³ at 4 m, produced a greater concentration than modelling the measured 1 m concentration of 110,000 µg/m³, however, the difference was only a factor of 2 (63.5 µg/m³ and 34.7 µg/m³, from the respective depths). Using the measured sub-slab concentration of 60,000 µg/m³, as the soil vapour input to the model, resulted in a predicted indoor air concentration of 29.8 µg/m³.

By applying the NEPM referenced shallow soil vapour to indoor air attenuation factor (α), of 0.01, derived from a statistical evaluation of numerous US based studies at chlorinated solvent sites, where α = indoor air concentration / shallow soil vapour concentration, an indoor air concentration of 600 µg/m³ was predicted. The prediction is substantially higher

than those of the model from the same soil vapour source. Predictions using a box dilution equation from measured diffusive mass flux through the warehouse floor, using the passive flux method, were essentially equal to measured indoor air concentrations (2.5 µg/m³ and 2.9 µg/m³, respectively) but dynamic flux under predicted indoor air slightly, possibly due to the differing time integration periods, 1 hour for the dynamic and 48 hours for the passive.

Table 1. Comparative predictions of indoor air concentration (TCE) using the J&E model in various modes, the NEPM attenuation factor, measured diffusive mass flux through the concrete floor and measured ambient air.

Vapour source or estimation method	Source concentration or mass flux	Predicted indoor air concentration
Modelled from groundwater at 5.5 m	380 µg/L	8.4 µg/m ³
Modelled from soil vapour at 4 m	450,000 µg/m ³	63.5 µg/m ³
Modelled from soil vapour at 1 m	110,000 µg/m ³	34.7 µg/m ³
Modelled from sub-slab vapour	60,000 µg/m ³	29.8 µg/m ³
From NEPM α factor of 0.01 (using sub-slab measured concentration)	60,000 µg/m ³	600 µg/m ³
Calculated from measured surface flux (dynamic chamber method)	5.6 µg.m ⁻² .h ⁻¹	0.93 µg/m ³
Calculated from measured surface flux (static chamber)	14.9 µg.m ⁻² .h ⁻¹	2.5 µg/m ³
Measured ambient indoor air concentration	2.9 µg/m³	

The health risk from the indoor air concentrations modelled or predicted were calculated after adjusting the concentrations for indoor commercial worker exposure. With respect to the carcinogenic effect of TCE, the risk is given by: Risk = Exposure Concentration x Unit Risk, where the World Health Organisation listed unit risk for TCE is 4.3 x 10⁻⁷. Using the enHealth (5) listed exposure factors, at an acceptable risk level of 1 x 10⁻⁵, the highest acceptable indoor air concentration of TCE is 157 µg/m³. Of the methods used to predict indoor air concentration, only one, the NEPM attenuation factor (α) exceeded that value.

CONCLUSIONS

Indoor vapour intrusion risk at an industrial warehouse with offices, was predicted using several methods. While the J&E model predicted indoor air concentrations to within one order of magnitude of the measured indoor air concentrations, the model uses algorithms for an ingress route that did not exist. The modelled VI prediction within a factor of 10 (from sub-slab) was thus fortuitous. Use of the NEPM attenuation factor vastly over predicted the indoor air concentrations. Surface flux (passive method) on the warehouse floor predicted indoor air concentrations approximately equal to the measured concentrations. It was concluded that in the absence of a perimeter 'crack' the main route for vapour intrusion was diffusion through the concrete floor and thus, diffusive floor flux accounted for most of the vapour intrusion pathway.

REFERENCES

- (1) NEPM Draft (April 2011) National Environmental Protection (Assessment of Site Contamination Measure. National Environment Protection Council.
- (2) CRCCARE. (August 2009) Technical Report No 13. Field Assessment of Vapours.
- (3) Heggie, A. C., Stavropoulos, B. (September 2010) Evaluating vapour intrusion risk using comparative dynamic and passive flux chambers at a TCE impacted site in Sydney, Australia. A&WMA Vapor Intrusion 2010.
- (4) Radiello Fondazione Salvatore Maugeri-IRCCS, <http://www.radiello.it/index.html>
- (5) enHealth Australian Exposure Assessment Handbook, Dec 2003. enHealth Council.

CASE STUDY: REMEDIATION COST MITIGATION THROUGH APPROPRIATE SOIL VAPOUR ASSESSMENT

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INTRODUCTION

Site works that investigate potential vapour intrusion resulting from volatile contamination in the sub-surface are becoming increasingly common within Australia. These investigations generally involve the collection of vapour phase samples in areas impacted by soil and/ or groundwater contamination to provide a direct measure of volatile impacts in the unsaturated soil profile. These data are then incorporated into vapour transport models as part of a site specific risk assessment.

Currently within Australia, the collection of soil vapour data is often limited to a small number of locations in areas of maximum impact, with this 'worst case scenario' data assumed to be present across the whole area to be assessed. In many cases, this extrapolation of the data can result in a significant overestimate of potential exposures and associated risks.

This case study presents a review of a site investigation and remediation project at a facility in Victoria, where collection of further data delineating the vapour impacts beneath the site would have resulted in a significant reduction in the scope of remediation works conducted at the site.

PRELIMINARY WORKS

An initial soil vapour investigation was conducted at a facility in Victoria to investigate potential vapour concentrations present above chlorinated hydrocarbon (CHC) impacts in groundwater. The investigation was carried out as the area was being refurbished, with an existing concrete floor slab to be removed and replaced. Three soil vapour bores were installed beneath the slab in proximity to known maximum groundwater dissolved phase impacts, with soil vapour data collected using six litre stainless steel canisters. The results indicated elevated concentrations of CHCs in the vapour phase, as summarised below.

Table 1. Summary of initial below-slab vapour data and comparison against ambient air and occupational exposure standards.

Chemical Detected	Maximum Concentration (mg/m ³)	Ambient Air Screening Criteria (mg/m ³)	Occupational Screening Criteria (TWAs) (mg/m ³)
Tetrachloroethene (PCE)	200	0.25	340
Trichloroethene (TCE)	2,500	0.023	54
Cis-1,2-Dichloroethene	900	0.063	793
Vinyl Chloride	30	0.0016	13

The need for an assessment of off-site migration of these impacts was thus identified, given the high concentrations detected, the potential for a release of vapours during slab removal, and the presence of sensitive off-site receptors 50 meters (commercial workers) and 100 meters (children) away.

A two dimensional air quality model (Ausplume) was utilised to model potential off-site migration of CHCs, assuming a potential worst case scenario of these impacts being present beneath the entire slab to be lifted. The modelled scenario indicated that exceedances of adopted ambient air screening criteria could occur at nearby off-site receptors.

FURTHER WORKS AND REMEDIATION

Rather than refining the assessment through the collection of further soil vapour data or using a more refined air quality model, priority was placed on active remediation to facilitate exacting maintenance schedules. A remediation project was therefore undertaken that included the installation of a soil vapour extraction system.

Field works conducted during the remediation phase confirmed that the assumptions that were initially applied to the assessment were indeed overly conservative and the vadose zone vapour extent present beneath the slab was confirmed to be only about 25% of the extent of the total slab reinstatement area.

CONCLUSIONS

Additional soil vapour sampling following the initial works conducted would have confirmed that the mass of contaminants present in the vapour phase beneath the slab was significantly less than initial conservative assumptions had indicated. Air quality modelling would also have confirmed that the potential for off-site migration of impacts would not have been a potential issue, given the reduced mass of vapour potentially released.

It was estimated that the performance of proposed additional vapour assessment works would have resulted in significant cost (approximately 30% of total remediation costs) and time savings to the client.

ENHANCING MASS RECOVERY RATES OF CHLORINATED SOLVENT CONTAMINATED SOIL WITH ADVANCED VOC CONDENSATION TECHNOLOGY DURING SOIL VAPOUR EXTRACTION

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INTRODUCTION

This paper presents the results of a scaled and phased approach to source remediation of high concentrations of recalcitrant chlorinated solvent compounds via soil vapour extraction (SVE) and vapour treatment at a Site in Southern California.

Phase I began with refrigerated condensation (C3) in order to achieve high mass removal rates to reduce lifecycle costs and time of remediation. The first two years (Phase I) resulted in recovery of over 92,000 pounds of mixed chlorinated solvents in the form of NAPL. The VOC constituents consisted primarily of MeCl, TCE, acetone, and isopropanol.

Phase II involves the installation of additional SVE wells in the source area and surrounding low-concentration VOC areas, and implementation of a dual-phase extraction system to treat source area groundwater. The vapours from both the vacuum extraction as well as the groundwater air stripping system from the source will be treated using a thermal oxidation system. The vapours from the SVE wells in the surrounding low-concentration VOC areas will be treated using GAC. A thermal oxidation system was selected in Phase II instead of a GAC system due to the presence of MeCl in the source area, which is not effectively absorbed by GAC. Phase II was used to manage long term venting.

Phase III will involve using a GAC system to manage diffusion limited asymptotic removal rates.

This case study review demonstrates the benefits of a phased approach, scalability in sizing systems, provides insight into off-gas treatment selection criteria for high concentration VOC or NAPL sites, and presents some available metrics and approaches for consideration of sustainability.

Contaminants of Concern

Chlorinated solvent impacts included but were not limited to MeCl, TCE, tetrachloroethene, acetone, isopropanol, vinyl chloride, cis-1,2-dichloroethene, 1,1,1- and 1,1,2-trichloroethane, trimethylbenzene, dichlorobenzene. Petroleum hydrocarbon impacts included benzene, toluene, ethylbenzene, and xylenes.

Target compounds for remediation and their concentrations were as follows:

- a. MeCl: 3.3 to 33,000 ppm (v/v)
- b. TCE: 5.8 to 21,000 ppm (v/v)
- c. Acetone: 12 to 6,400 ppm (volume/volume)
- d. Isopropanol: 12 to 6,000 ppm (v/v)

Site Geology

The geology and hydrogeology of the site can be summarized as intercalated sands and silty sands separated by competent silt and clay horizons. The geological formations present

beneath the site are illustrated in Figure 1 Conceptual Site Model. Groundwater is present at the site at approximately 10 meters below ground surface (m bgs).

METHODS

The vapour extraction was initially accomplished using existing SVE wells installed at approximately 50-foot intervals and located within the estimated confines of source area. Each well was dual-nested, with a shallow screened interval from approximately 3-6 m bgs and a second interval from approximately 8-10 m bgs. The extraction system was subsequently expanded after 9 months of operation to add seven new dual-nested SVE wells and to expand the capabilities of the system.

RESULTS AND DISCUSSION

Phase I performance resulted in the removal efficiency for VOCs, including TCE and MeCl, at near 100 percent. The system removed approximately 92,000 pounds of VOCs (including 21,000 pounds of TCE and 56,000 pounds of MeCl). These quantities were calculated by averaging the influent vapour concentrations collected during monthly sampling events and assuming that these average concentrations remain constant between the two sampling events. The calculation for VOC mass removed is equivalent to approximately 6,800 liters of TCE and 19,300 liters of MeCl. Removal efficiency and VOC mass removal by the SVE system was calculated for total VOCs, TCE, and MeCl, using laboratory analytical data and estimated system flow rate measurements.

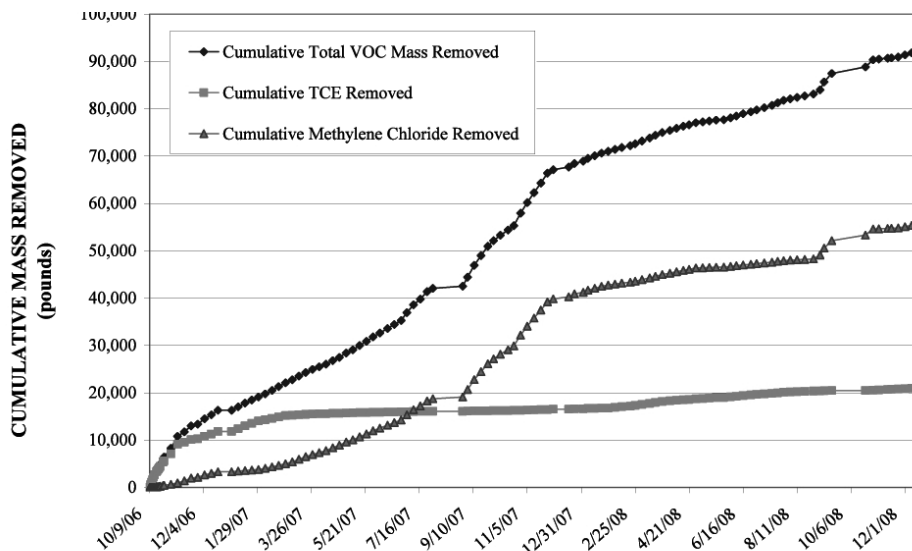


Figure 1. Cumulative Mass Recovered

The graph reveals influent total VOC vapour concentrations collected from the system. Total VOCs, TCE, and MeCl are based on laboratory analytical data.

CONCLUSIONS

During Phase I, the refrigeration condensation system had an operational uptime of 93.5% over a 27-month period and operated in full compliance with the air quality operating permit conditions. The treatment efficiency of the refrigeration condensation system was near 100 percent with minimal carbon usage. The system ran for approximately 16,881 hours and removed approximately 92,000 pounds of VOCs. The C3 units produced approximately 63,455 gallons of condensed liquid, which was transferred into an onsite above ground storage tank and disposed off-Site. The maximum TCE concentration recorded at the site reduced from 21,000 ppmv to 290 ppmv and the maximum MeCl concentration reduced from 33,000 ppmv to 340 ppmv.

CONFIRMATION OF THE USE OF INNOVATIVE SITE ASSESSMENT TOOLS – XRAY FLOURESCENCE

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INTRODUCTION

In order to expedite the site assessment process for a site with the primary contaminant being arsenic (As), a portable hand held X-ray Florescence (XRF) device was utilised to gather data insitu.

Significant effort was also expended to confirm the results of the X-ray fluorescence testing through submission of duplicate soil samples to a NATA registered laboratory for analysis to provide ease of comparison.

This paper examines the results of the XRF testing against that of laboratory analysed samples in various soils types to assess the agreement of the field methodology versus laboratory methods and compares the methods for time, cost and logistical benefits.

METHODS

The use of XRF for field testing was reviewed by the authors prior to selection of the appropriate XRF and its applicability to the soils and contaminants expected.

The assessment site comprised an area of historical mining tailings with arsenic being the key contaminant of concern within typically clayey soils and mine tailings.

The method of site assessment incorporated sampling via testpitting and hand augering, with sample density determined based upon current and proposed use of the site. Specific sampling was determined at the sampling location aimed at determining contaminant concentrations within all soil and fill types identified at the particular location. A strength of the XRF sampling technique allowed for the analysis of multiple representative depths through the sampling point.

RESULTS AND DISCUSSION

Detailed analysis of the results of XRF sampling versus laboratory analytical results was conducted for the assessment site.

Initially, all XRF and laboratory analytical results were compared. A total sample size of 39 samples are available for the comparison. Results are provided in Figure 1.

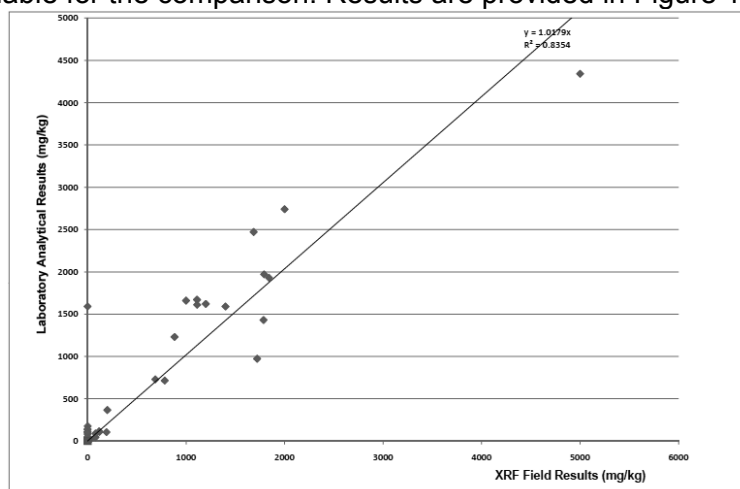


Figure 1. Comparison of all XRF versus Laboratory Analysis Results - Arsenic

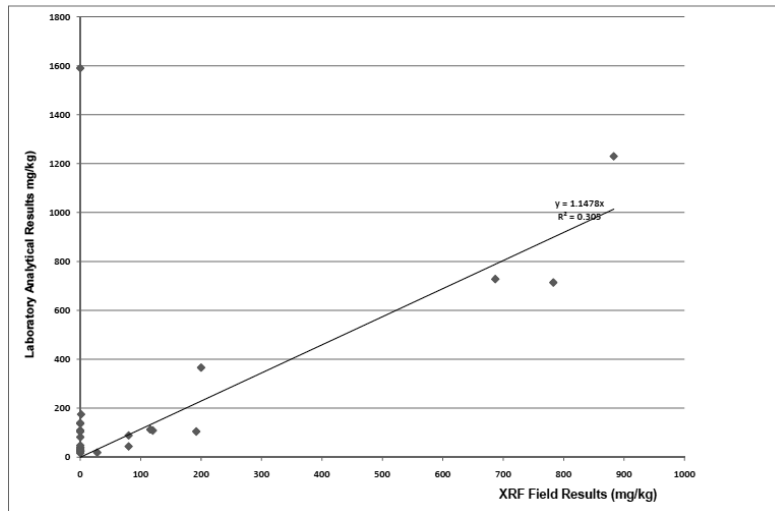


Figure 2: Comparison of XRF results and Laboratory Analytical results less than 1,000 mg/kg

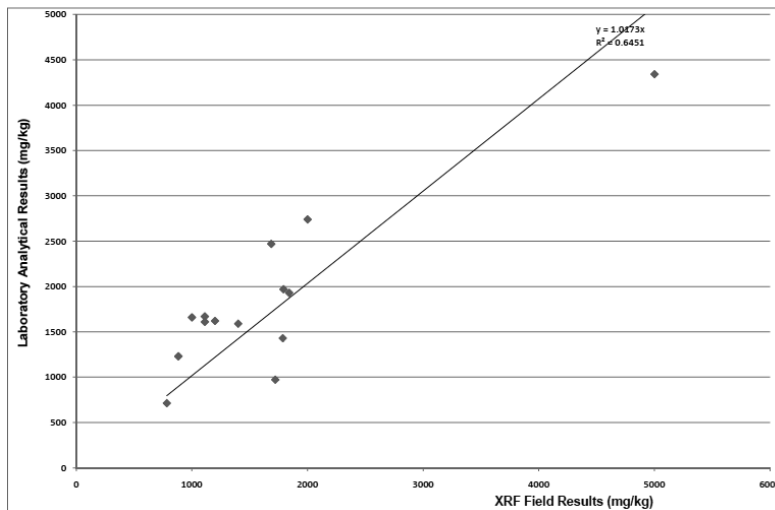


Figure 3: Comparison of XRF results and Laboratory Analytical results greater than 1,000 mg/kg

CONCLUSIONS

As a direct comparison the results appear to be quite acceptable, within the ranges of sample uncertainty. Closer inspection of the data was completed with results below 1000 mg/kg and above 1000 mg/kg reviewed further. The results suggest that for those results below 100 mg/kg the XRF loses accuracy, however for results above 100 mg/kg, the XRF generally produces results that can be relied upon for rapid assessment and decision making.

Use of the XRF allowed decision making in the field to:

- Understand the key strata containing elevated Arsenic concentrations, ie what to look for
- Select samples for laboratory analysis to maximise value for money
- Select samples for leachability testing
- Select the soil strata in which to conduct bioavailability testing

USING REAL TIME TOOLS TO DEVELOP HIGHER QUALITY CONCEPTUAL SITE MODELS

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INTRODUCTION

High resolution site characterization is an efficient process for developing rigorous conceptual site models (CSMs) (i.e., defining subsurface hydrogeologic conditions, contaminant distribution, and potential risk pathways) through the application of proven scientific principles, investigation approaches, and site characterization tools. This approach significantly reduces uncertainty and enables development of sustainable solutions to address subsurface contamination issues.

To achieve this objective, a variety of screening tools are used to collect large volumes of data in a cost effective manner, which enables definition of source area and plume architecture (Fiacco et al. 2005). Once this has been completed, a relatively small number of soil, groundwater, and/or soil gas samples are collected from strategically selected locations for quantitative analysis using a certified laboratory. Collectively, these data are known as a collaborative data set.

Once developed, an improved CSM allows for more effective assessment of human health or ecological risk. This provides for better decision making and reductions in business risk, stakeholder concerns, and life-cycle costs.

This poster describes some of the direct push, real-time tools available in Australia and presents outcomes of field investigations conducted using these tools, as well as some of the CSMs developed using these tools.

DISCUSSION

Membrane Interface Probe

The Membrane Interface Probe (MIP) is a direct push, real-time, direct sensing tool that provides continuous semi-quantitative data on the distribution of volatile organic compounds (VOCs) in the subsurface. The probe on the MIP is equipped with a porous polytetrafluoroethene membrane set into a steel plate that is heated electrically to volatilize organic compounds present in the soil and/or groundwater adjacent to the tip. Depending on the molecular size, some VOCs pass through the membrane by diffusion under a concentration gradient. Once a compound has passed through the membrane it enters a sampling stream of inert gas which carries it to detectors at ground surface. A variety of detectors can be employed using the MIP, including a photoionization detector (PID) to measure aromatic compound, a dry electrolytic conductivity detector (DELCD) to measure chlorinated compounds, a flame ionization detector (FID) to measure petroleum hydrocarbons, chlorinated solvents and methane and an electrical conductivity (EC) dipole array, to measure the electrical conductance of the soil and fluids in the soil. A real-time continuous profile of the results from these detectors versus depth is then developed.

MIP results have been used at numerous sites in US (Ravella at al., 2007) and Europe to define the three-dimensional source area architecture or the location of plume cores within two-dimensional cross sections.

Laser Induced Fluorescence

The Ultra-Violet Optical Screening Tool (UVOST®) Laser Induced Fluorescence (LIF) is a direct push, real-time, semi-quantitative and qualitative direct sensing tool that uses ultra-violet laser light to cause fluorescence in Light Non-Aqueous Phase Liquids (LNAPLs), which

can then be measured (CRC-CARE 2009). The tool is affixed at the head of a Geoprobe® drill rod string. Laser light is sent through a fiber optic cable placed within the Geoprobe® rods where it exits a sapphire window and strikes the soil matrix as the probe is steadily pushed into the ground. The fluorescence emitted by soil is collected by a second sensor and transmitted via fiber optic cable back up the bore hole to the instrument for detection and analysis. This allows for a continuous profile of fluorescence versus depth to be developed. LIF results were combined with other data streams (eg, soil type, permeability, laboratory analytical data) to develop cross sections or combined logs to better depict the distribution of LNAPL in the subsurface in active petroleum retail sites located in Victoria, New South Wales and South Australia. The waveforms observed were used to distinguish different LNAPL signatures (which result from different products being present or differing degrees of weathering). This tool has been proven to be particularly useful in developing a more refined understanding of LNAPL source zones and migration pathways, which can often be misrepresented when relying solely on observed LNAPL thicknesses in monitoring wells. While the use of this tool can not differentiate between residual and mobile LNAPL, it has been adopted to provide a line of evidence to support mobility assessment using more traditional means (eg, LNAPL baildown testing).

Geoprobe® Hydraulic Profiling Tool

The Geoprobe® Hydraulic Profiling Tool (HPT) is a direct-push, real time, semi-quantitative tool that is used to evaluate hydraulic properties of unconsolidated soils. The HPT probe is equipped with a small stainless steel screen that is used to inject water at a constant low flow rate into the formation as the probe is advanced into the subsurface. Injection pressure, which is monitored and plotted with depth, is an indication of the relative hydraulic properties of the soil. The HPT probe is also equipped with an EC probe to measure electrical conductance of the soil and fluids in the soil.

The combination of relative permeability and EC data was used to develop a continuous profile of stratigraphic and hydrostratigraphic changes in real time at active petroleum retail sites in Victoria and South Australia. These data were calibrated by a small number of confirmatory soil borings to extrapolate the findings to wider areas across the sites. The use of these calibrated representations of site geology and hydrogeology have proved to be effective, especially when combined with other data sets such as LIF or MIP, to depict plume architecture and identify perched water bearing zones using 3D geological modelling software packages.

CONCLUSIONS

Data collected using MIP, LIF and HPT were used to characterize areal and vertical extent of contamination as well as the site stratigraphy, which were collectively used with a limited number of “calibration” samples to develop detailed CSMs at various sites. These CSMs have been used to support effective decision making in contaminated site management projects throughout Victoria and South Australia.

REFERENCES

- Fiacco, R.J., J. Frazier, M. Ravella, S. Pitkin and M. Rossi (2005) An integrated toolbox approach to characterize heterogeneous overburden environments, Consoil 2005, Bordeaux, France.
- Ravella, M., R. J. Fiacco, J. Frazier, D. Wanty, and L. Burkhardt. (2007). Application of the membrane interface probe (MIP) to delineate subsurface DNAPL contamination, *Environmental Engineer*, 43(1), pp. 26-30.
- CRC-CARE (2009) Characterisation of Sites Impacted by Petroleum Hydrocarbons. National Guideline

STABLE ISOTOPE PROBING TO DOCUMENT BIODEGRADATION UNDER MONITORED NATURAL ATTENUATION CONDITIONS

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INTRODUCTION

Depending on site conditions including contaminant concentrations, availability of electron donors or acceptors, groundwater velocity, and proximity to potential receptors, monitored natural attenuation (MNA) can be an effective remediation strategy. However, MNA is sometimes viewed as a “do nothing” solution in which decreases in contaminant concentrations result from physical processes (e.g. dilution) rather than biodegradation. Ultimately, the feasibility and regulatory acceptance of MNA as a remediation strategy rests upon demonstrating contaminant biodegradation under existing site conditions.

Stable isotope probing (SIP) is an innovative method to track the environmental fate of a “labelled” contaminant of concern to unambiguously determine whether biodegradation is occurring and evaluate the feasibility of MNA. With the SIP method, a Bio-Trap[®] sampler is baited with a specially synthesized form of the contaminant containing “heavy” carbon (¹³C). When the baited Bio-Trap is deployed in a monitoring well, the ¹³C labelled contaminant is subject to the same physical, chemical, and microbiological processes as the unlabelled contaminant present at the site. If biodegradation is occurring, the ¹³C label from the synthesized contaminant in the Bio-Trap will be incorporated into the end products of biodegradation: microbial biomass and dissolved inorganic carbon (CO₂)

This presentation focuses on case studies in which SIP was performed to evaluate MNA at sites impacted by gasoline (benzene), fuel oxygenates (MTBE), diesel components (naphthalene), and other industrial contaminants (aniline, nitrobenzene, chlorobenzene).

METHODS

Bio-Trap samplers were amended with ¹³C labelled contaminants of concern and deployed in existing monitoring wells in the dissolved plume for 30 to 90 days. Briefly, Bio-Traps are passive sampling tools that collect microbes over time for the purpose of better understanding biodegradation potential. Bio-Traps contain Bio-Sep[®] beads, an engineered composite of Nomex[®] and powdered activated carbon (PAC) that provides a large surface area for microbial colonization and biofilm formation. Due to the PAC component of the Bio-Sep beads, Bio-Traps can be “baited” with ¹³C labelled compounds by vapour phase adsorption. During field deployment, biofilms characteristic of in situ aquifer conditions are formed on and within the Bio-Sep beads (Busch-Harris et al., 2006, Sublette et al., 2006 and 2008). Following field deployment, the Bio-Trap[®] is recovered and two methods are used to conclusively demonstrate biodegradation of the contaminant of concern:

- (a) Quantification of ¹³C enriched phospholipid fatty acids (PLFA) indicates contaminant incorporation into microbial biomass.
- (b) Quantification of ¹³C enriched dissolved inorganic carbon (DIC) indicates contaminant mineralization.

RESULTS AND DISCUSSION

At gasoline impacted sites, benzene is often the contaminant of principal concern due to its known toxicity, mobility, and slower rates of biodegradation under anaerobic conditions typical of MNA. Bio-Traps amended with ^{13}C labelled benzene were deployed in select monitoring wells at gasoline contaminated sites where MNA was being considered as a remediation alternative. Based on traditional groundwater monitoring data, subsurface conditions at the sites were similar in terms of contaminant concentrations and redox state. SIP results and thus the feasibility of MNA at the sites, however, were markedly different (Figure 1).

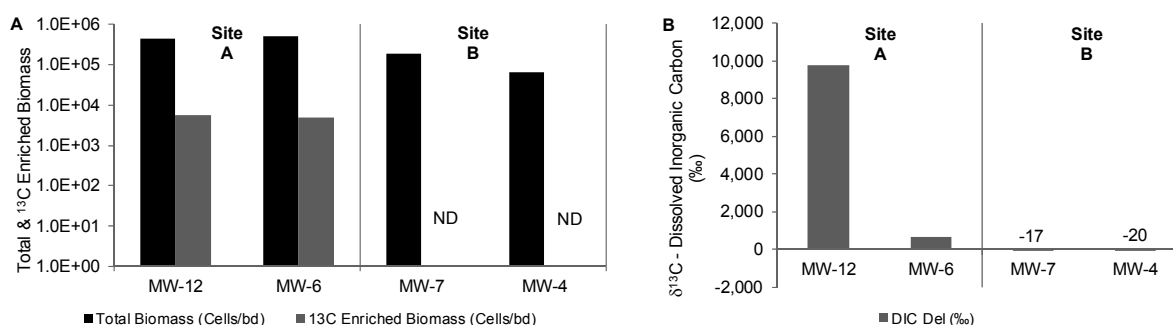


Fig. 1. (A) Quantification of total and ^{13}C enriched biomass. (B) Quantification of ^{13}C enriched dissolved inorganic carbon (DIC). Bio-Traps were amended with ^{13}C labelled benzene and suspended in existing monitoring wells for approximately 30 days prior to recovery and analysis.

At Site A, substantial incorporation of ^{13}C into biomass ($\sim 10^3$ enriched cells/bd) at both monitoring wells demonstrated benzene biodegradation under existing site conditions. Although lower at MW-6 than at MW-12, detection of ^{13}C enriched DIC in both wells at Site A documented mineralization of benzene. Conversely, neither ^{13}C enriched biomass nor DIC was detected in study wells at Site B. In terms of site management decisions, the SIP results indicated that MNA may be a feasible remediation strategy at Site A but enhanced remediation alternatives should be considered at Site B.

CONCLUSIONS

For a broad spectrum of common contaminants of concern, SIP can provide the unequivocal evidence of in situ biodegradation required to evaluate the feasibility and performance of MNA as a site remediation strategy.

REFERENCES

- Busch-Harris, J., Jennings, E., Sublette, K. L., Roberts, K. P., White, D. C., Peacock, A., Davis, G., Ogles, D., Holmes, W. E., Yang, X., Kolhatkar, A., Beckmann, D., Kolhatkar, R. (2006) Monitoring subsurface microbial ecology and demonstrating *in situ* biodegradation potential using Bio-Sep Bio-Traps. *Ecol. Chem. Eng.* 13:349–372.
- Sublette, K. L., Peacock, A., White, D. C., Davis, G., Ogles, D., Cook, D., Kolhatkar, R., Beckmann, D., Yang, X. (2006) Monitoring subsurface microbial ecology in a sulfate-amended gasoline contaminated aquifer. *Ground Water Monit. Rem.* 26:70–78.
- Sublette, K. L., Busch-Harris, J., Roberts, K., Landrum, C., Peacock, A. D., Davis, G., Ogles, D., Holmes, W., Ota, C., Yang, X. (2008) Bio-Traps coupled with molecular biological methods and stable isotope probing demonstrate in situ biodegradation potential of MTBE and TBA in gasoline-contaminated aquifers. *Ground Water Monit. Rem.* 28:47–62.

PLUGGING THE GAPS: A GROOVY CONCEPTUAL SITE MODEL AND HOW TO VALIDATE IT

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Introduction

A well-stocked toolbox of advanced site investigation tools was used to validate an unusual conceptual site model in a natural attenuation feasibility study and provided the key information needed to manage a two kilometre plume of chlorinated hydrocarbons (CHC) in Hanover, Germany. The five year study (2003-2007) was funded through 'KORA', a priority of the German Federal Ministry of Education and Research. Having initially characterised the plume sufficiently, the next step was to identify and quantify natural attenuation processes taking place in the aquifer, which consists of quaternary gravels and sands above an undulating surface of Cretaceous mudstones. The plume is detached from the contamination source, a former chemical wholesale company, which was safeguarded by a slurry wall more than 10 years ago supporting the additional pump and treat measures. Degradation products of trichloroethene make up the bigger part of the CHC contaminants today, with their highest concentration near the base of the shallow aquifer where groundwater flows approximately 100 metres per year in a westerly direction towards the Leine River. Ultimately the output of this work was to provide model-based advice on the future management of the site, based on an estimate of remaining contaminant mass and attenuation rates. From a regulatory viewpoint it was essential that the local authority, which is also the site owner, be provided with a planning tool to efficiently manage all affected issues in connection with water abstraction, water right licences or building permits. Hence key information needed would include the mobility of the plume and when permissible levels of contamination will be achieved without further active measures.

Project Objectives

- Hydrogeological site investigation through historic research, detailed soil borings with monitoring well installation, direct-push investigation in hard to access areas and geophysical assessment methods.
- Monitoring to establish groundwater composition, quality (annually) and dynamics (quarterly) with special consideration for reproducibility. Tests of innovative methods, e.g. particle tracking, passive sampling methods, desorption column tests with spiked contaminants).
- Groundwater analyses for contaminants, their breakdown products, the inorganic composition, dissolved gases and stable isotopes.
- Geochemical characterisation of sediment samples for evaluation of reactive compounds.
- Modelling of geology, hydrogeology, degradation rates and groundwater flow.
- Development of a robust conceptual site model (CSM) and prediction of natural attenuation processes.
- Estimation of time frame when passive management could be implemented.

Description of works

After reviewing the historic plume data (beginning in the 1970s) and geological information a very basic CSM was outlined and then refined with data of an initial groundwater sampling round. The plume appeared to be highly unusual in terms of distribution of CHC metabolites. The most progressed breakdown of contaminants was found in the upstream part of the plume and adjacent to the safeguarded source, where vinyl chloride along with reducing

groundwater conditions dominated. The source contaminant trichloroethene (TCE) along with oxidizing conditions was found at the downstream end of the plume. Considering these unusual findings the CSM was christened the “inverse plume”. To verify the CSM, data gaps were addressed with model based decision tools. Redress of the biggest gaps was prioritized and timelined in three field campaigns of drilling and well installation. As the plume area is set below a densely populated urban area, the refining of the CSM by conventional measures became more difficult as the project progressed, due to sheer lack of space to put in drill holes. After the completion of the three drilling campaigns, yielding 60 monitoring wells in 20 groups with short screens (2-3 m), the monitoring network featured 120 depth differentiated wells in the plume area, up- and downstream and cross-gradient. In the CSM, a quaternary channel structure in the upstream was thought to act as a secondary source area due to residual CHC remaining in the deepest part of this part of the aquifer. Even more 3D geological and chemical data were necessary to clarify this supposition, but again due to space limitations a classical drilling approach was not feasible. To fill these spatial gaps a combination was used of an innovative non-intrusive approach combined with seven near surface shear wave seismics (“land streamer”) profiles of a total 2.8 km length. Vertical seismic profiles and direct push electric conductivity logging and groundwater sampling was utilized to calibrate and correlate data. The combined results were used to map the channel and refine the spatial accuracy of the hydrogeological model. The deepest parts of the channel system were targeted for separate phase (DNAPL) testing. However, no evidence for DNAPL was found, hence a different secondary source must have been active. Column desorption tests with ¹⁴C-spiked 1,2-cis-DCE delivered the key enhancements to the degradation and flow model: the retardation factors and the sorption/desorption kinetics. The application of the refined model demonstrated to the local authorities that the only economically sensible remediation strategy, Monitored Natural Attenuation, is sustainable and environmentally sound.

Conclusions

- Development of the CSM was based on many factors including historic data evaluation, but a thorough hydrogeological and geological understanding was essential.
- Refining the geological and hydrogeological aspects of the CSM was done by applying near surface seismics to a key plume area.
- For best results the non-intrusive tool shear wave seismics needed to be calibrated with existing data and cross validated with EC logs and vertical seismic profiles.
- The combination of conventional techniques (eg drilling, sediment sampling, sampling of groundwater monitoring wells) and innovative methods used successfully removed the data gaps.
- The new dataset improved aspects of the CSM which led to a more robust decision making tool.
- The land streamer application is a valuable tool for non-destructive near surface site investigations.
- No evidence of historic CHC migration was found in the quaternary channel – the initial model assumption was rejected.
- Column tests delivered the kinetics for the refined fate and transport model and the key piece for the final CSM.
- Gap analysis and redress is an ongoing process – CSMs need regular updates as more data evolve.

This project was part of the funding priority “KORA” of the German Federal Ministry of Education and Research.

References

KORA - Kontrollierter natürlicher Rückhalt und Abbau von Schadstoffen bei der Sanierung kontaminierter Böden und Grundwässer’ (Retention and Degradation Processes to Reduce Contaminants in Groundwater and Soil). <http://www.natural-attenuation.de/content.php?lang=en>

FIRE DAMAGED ASBESTOS: CASE STUDY PART TWO - REMEDICATION OF ASBESTOS IN SOIL

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INTRODUCTION

At CleanUp 09, we presented the initial characterisation and remedial design for the former Patea Freezing Works. This paper presents the subsequent clean-up that has allowed the site's beneficial reuse.

The former Patea Freezing Works in the Taranaki Region of New Zealand began as a canning plant and tallow factory in the late 1800s. In 1904 freezing technology was introduced and the factory was in continuous operation until its closure in 1982. In February 2008, a number of prominent buildings on the site were destroyed by fire, leaving twisted metal and piles of ash and asbestos from a legacy that spanned almost 100 years.

The asbestos was primarily used in fibre cement sheeting within the building structures but was also present as friable lagging in the boiler house. Smoke from the fire blew over the town prompting authorities to evacuate the small township as they were fearful of exposure to asbestos potentially present in the smoke carried by strong onshore winds. Fragments of Asbestos Containing Material (ACM) was scattered over a large area of the site from the fire.

OBJECTIVES

After the emergency response, the South Taranaki District Council (STDC) was faced with the task of clean-up. AECOM was engaged to develop a remedial strategy, oversee the remediation works and provide validation services to return the site to a condition suitable for future agricultural and/or recreational land use.

This case study illustrates how the clean-up objective was achieved using the Western Australian (WA) Department of Health (DOH) Guidelines (May, 2009), in close consultation and collaboration with STDC and Taranaki Regional Council (TRC).

REMEDIAL STRATEGY

Based on initial contamination characterisation, the preferred option was to remove the top layer of ACM impacted soil and place this waste in an engineered containment cell on the site. This option, however, could not be used because of local cultural objections and competitive landfill disposal pricing. As a result, the "dig and dump" option was adopted. Onsite treatment of non friable ACM soil became an important consideration of the remediation to ensure the success of this off-site removal option. Consideration was also given to other potential contaminants of concern – both organic and inorganic.

Remediation commenced in November 2009 and the majority of the works were completed by June 2010. Remediation comprised screening of ACM impacted surface soils, onsite disposal of ACM impacted deeper soils and off-site disposal of Fibrous Asbestos (FA) and Asbestos Fines (AF) impacted soils and waste.

Under the DOH 2009 guidelines, ACM is defined as material where asbestos is bound in a matrix and cannot pass through a 7mm x 7mm sieve; FA is defined as friable material including weathered ACM and loose fibrous material; AF is defined as free fibres or fibre bundles of asbestos and ACM that can pass through a 7mm x 7mm sieve.

Treatability Trail

Approximately 2,620 m³ of soil was successfully treated and re-used onsite. Soil was treated using a grizzly screener which segregated the soil/waste into different categories. The waste was treated wet to prevent asbestos fibres becoming airborne.

The material to be screened was segregated by previous land use and sampled prior to and subsequent to screening. Pre-screening samples were to confirm the material's suitability for screening. Post-screening samples were to identify if the mechanical screening process created AF (ACM <7mm) or FA. The presence of AF and/or FA above adopted threshold levels (DOH 2009) precluded the material for beneficial re-use onsite.

Results of the trial showed that approximately 10% of the clean material could not be re-used due to concentrations of AF and FA above the adopted criteria (DOH 2009). The trial was successful to justify continuation of the screening program to full scale; however it was necessary to continue the pre and post sampling throughout to validate the method.



Fig. 1. Screening Trial Underway at Patea.

In general, challenges to the successful treatment of Patea's ACM impacted soil included:

- (a) Age and condition of the ACM fragments
- (b) Presence of other contamination (eg lead)
- (c) Moisture content of the soil and prevailing weather conditions
- (d) Silt and clay content of the soil
- (e) Professionalism and control of the screening, including stockpile validation

Variables that influence the success of mechanical screening include how readily AF and FA are liberated from ACM fragments, the level of agitation of the matrix during screening, and the ratio of clean soil versus ACM impacted waste produced.

VALIDATION

Validation comprised a combination of visual inspection, photographic record, surveying of onsite storage cells and inaccessible areas, grid based soil sampling across the site, capping of the site with a layer of clean fill, and the monitoring of groundwater along the down gradient boundary to the Patea Estuary. The monitoring wells were installed to address potentially mobile organic and inorganic contaminants from the historic industrial activities.

CONCLUSIONS

The former Patea Freezing Works was remediated with the application of the WA DOH, Guidelines, in close consultation and collaboration with the local regulatory agency (TRC). Adoption of these guidelines meant that previous seemingly insurmountable challenges could be overcome whilst still achieving the cleanup objectives for the site.

REFERENCES

WA Department of Health (DOH 2009). *Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia*. Toxicology Branch, Environmental Health Directorate, Department of Health, May 2009.

COMPOSITE SAMPLES: DO THEY OFFER VALUE WHEN CONSIDERING AVERAGE EXPOSURE CONCENTRATION OVER DECISION AREAS

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INTRODUCTION

Assessment of large potentially contaminated sites subject to subdivision presents a challenge when designing an appropriate sampling strategy. Current Australian guidance, such as NSW EPA (1995) Sampling Design Guidelines or AS4482.1, use statistical hypothesis testing, on absence of a circular hot spot of specified size, as means to guide sampling design. In many situations the assumptions in this guidance is no applicable, particularly when the presence of heterogeneous fill is identified on a site. For larger sites the hot spot defined in the guidance can occupy several blocks in the proposed subdivision. Therefore deciding on an appropriate sampling approach in light of current guidance needs to recognize that confidence in the site characterization can be low, even when adopting the recommended number of samples, particularly in situations where historical information on land use is limited and / or fill is present. There are several options for design of a sampling approach, including individual samples for back yard area or composite samples.

When dealing with subdivision sites, one important consideration in relation to human health is the average exposure concentration. Acknowledging the limitation of the current guidance on hot spot based sampling some approaches used include collection of an individual sample in each back yard or use of composites either over several lots or on an individual lot basis. To date only very limited work has been done to assess the relative performance of these approaches.

METHODS

To assess the performance of the individual sample and composite sample approaches lead concentration data from an intensive sampling program from 5 properties in a mineralised area was used to assess their performance. Table 1 presents a summary of the data generated from the sampling and analysis program. As shown the data for Properties 1, 2 and 5 show a slight positive skew, while data for Properties 3 and 4 appeared more normally distributed.

Table 1: Summary of data set

	No	Mean	Median	Standard Deviation	Minimum	Maximum
Property 1	118	805	516	1094	59	9830
Property 2	80	848	589	941	16	4609
Property 3	46	985	938	1032	115	2034
Property 4	60	1000	940	708	9	3374
Property 5	56	1040	773	857	64	5134

The assessment of performance included simulated collection of a range of samples including:

- An individual sample from the centre of each back yard;
- A three part composite from three randomly selected locations in each backyard;
- A five part composite from five randomly selected locations in each backyard;
- A ten part composite from ten randomly selected locations in each backyard;

RESULTS AND DISCUSSION

The results of the assessment are presented in Table 2, along with the mean concentrations calculated for the entire data set. The greatest variability appears to be between the individual sample and the population mean. To assess relative performance between the methods, the relative percent difference between the method results and population mean was also calculated and results are presented in Table 3.

Table 2: Summary of sampling results

	Single Sample	3 Part Composite	5 Part Composite	10 Part Composite	Population Mean
Property 1	2815	1335	781	767	805
Property 2	346	875	1538	516	848
Property 3	1040	949	880	1018	985
Property 4	1097	852	903	851	1000
Property 5	1120	1853	712	1208	1040

Table 3: Summary of relative percent difference results

	Single Sample	3 Part Composite	5 Part Composite	10 Part Composite
Property 1	56%	25%	-1%	-2%
Property 2	-42%	2%	29%	-24%
Property 3	3%	-2%	-6%	2%
Property 4	5%	-8%	-5%	-8%
Property 5	4%	28%	-19%	7%

As Table 3 illustrates, the relative percent differences for the individual sample approach shows an excessive differences. Two elevated differences were also apparent for the three and five part composite tests, although the differences were less pronounced. Overall the ten part composites provided the closest estimate of the population mean, with only one sample showing an elevated difference. Thus when considering the areas of interest where exposure can occur in a subdivision, composite samples, particularly those comprised of multiple parts, can offer a reasonable estimate of the potential mean exposure concentration. Use of an approach involving individual samples is associated with a risk that the sample is not representative of the average concentration in the backyard.

CONCLUSIONS

Given that existing guidance based on the circular hot spot approach there is a high risk of missing contamination that spreads across an entire backyard for larger properties proposed for subdivision. Use of alternative approaches was considered. Performance of some alternative approaches to assess these exposure areas of interest simulated collection of individual samples from the centre of the yard and a series of composite samples was used.

Results indicated that use of an individual sample can result in a risk of that sample not being representative of the average exposure concentration. Three, five and ten part composite samples showed less difference with the population mean, with 10 part composite samples performing best. Under these types of composite approaches there would not be a need to adjust the assessment criteria as the aim is to assess the average exposure concentration of humans over the backyard area. As such use of composite samples offers an economic means of collecting relevant data from backyard areas to estimate average exposure concentration for humans. This may then provide a means of decreasing the uncertainties in relation to assessing large sites and an alternative to the hot spot based approach.

THE ROLE OF NUMERICAL FLOW AND TRANSPORT MODELS AS DECISION SUPPORT SYSTEMS IN REMEDIATION PROJECTS

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INTRODUCTION

Contaminations of the environment by toxic or harmful substances are often characterised by very long self-remediation time frames. If a contamination potentially or actively harms a subject of protection, clean-up or safeguard operations may become inevitable. Measures for an exhaustive removal (if possible at all) on a short timescale typically require high technical and consequently monetary effort. Therefore, investing into a sound comprehension of the underlying processes can already be remunerative even if only incremental improvements of a clean-up strategy can be achieved. Numerical models have proven to be an appropriate tool to optimize remediation or safeguard strategies.

CASE STUDIES

A number of projects have been conducted showing that the best remediation or containment strategy must be found for each case individually. The studies have been motivated by management targets for different operations, including

- (a) water supplies
- (b) mine tailings
- (c) large construction sites.

DECISION SUPPORT BY NUMERICAL MODELS

Groundwater flow is typically the dominating process for the propagation of contaminants in the subsurface. In many practical projects, the comprehensive understanding of the groundwater flow system has been the key to find an effective and cost-efficient treatment or containment strategy.

Numerical models have been applied in a number of possible roles, where they have substantially supported the decision-making process and contributed to the development of cost-saving remediation strategies. This includes

- (a) comprehension of relevant natural processes
- (b) evaluation and comparison of different remediation approaches (scenario analysis),
- (c) dimensioning of underground and overground plants and installations
- (d) design of monitoring systems
- (e) supply of a data basis for governmental approval processes

CONCLUSIONS

Numerical flow and transport models have been proven to be valuable tools for understanding flow and solute-transport processes at and around contaminated sites. By respecting the local hydrogeological conditions, optimized and cost-efficient solutions for clean-up or safeguard projects have been found.

BEFORE AND AFTER PURGE SAMPLING: IS THERE ANY DIFFERENCE?

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INTRODUCTION

Current guidelines for groundwater sampling indicate that a well must be purged a minimum of three to four bore casing volumes or pumped continuously until parameters such as pH, electric conductivity and temperature reach stable values (USEPA, 1986). The rationale is that purging removes stagnant water from the well prior to sampling and consequently provides a representative sample of the aquifer. In literature, many authors (Varljen et al., 2006) have affirmed that the amount and rate of well purging depends on the hydrogeology of the site. Given the stipulation of well purging before a sample can be taken, it is important to have some basis for determining the volume of water that needs to be purged, or the duration of the purge. In the current study, an attempt is made to evaluate well purging criteria and to study the need for purging of wells for representative samples from a contaminated site located in Edinburgh, SA, Australia. This evaluation aims to establish the number of well-volumes required to obtain stable field parameters and correlate them to concentration values, in order to determine the optimal bore volumes required to obtain representative samples. A methodology, which is a combination of both low flow and volume purging, is implemented to purge the wells.

METHODS

The sampling method used in this study is a combination of both low flow and volume purging. In this method, the pump is placed 1 m above the bottom of the well (i.e. inside the screen) and started at low speed, and the water table is maintained at a specific depth by increasing or decreasing the flow rate. This (i.e. steady state conditions) is particularly important for several reasons: it indicates that the well is not pumped dry, steady flow into the well is maintained, which is a main requirement in low-flow purging; minimises drawdown of the static water table and draws the water directly from the formation. The pumping rate adapted to each monitoring well was recorded. Samples were collected before purge, at specific pumped volumes and at the end of the purge. Field parameters which included: dissolved oxygen (DO), electrical conductivity, pH, temperature, redox potential (ORP) and turbidity were continuously monitored using a flow cell and multiple probes (Aquaread AQUAPROBE) dedicated to this purpose.

RESULTS AND DISCUSSION

The study area covers approximately 1800 ha of land and is located 25 km north of Adelaide central business district. The site, originally farmland, was developed into a manufacturing facility. Several potentially contaminated areas have been identified within site due to historical related activities. Contaminants detected in the ground water include chlorinated hydrocarbons, among which TCE is predominant and low but significant levels of hexavalent chromium, which can retard or prevent natural attenuation of TCE in groundwater. The site is located on the lower Adelaide Alluvial Plain comprising two main Quaternary aged units: the Pooraka Formation and the Hindmarsh Clay. The depth of the aquifer is approximately 11 to 14.5 m below surface. Soil permeability ranges between 0.233 to 0.259 m/day. The mean hydraulic gradient in the study area varied from 0.00075 to 0.005, with a mean value of

0.0025. The groundwater flow is from west to north-west and flow direction remains largely stable.

Figure 1 shows TCE concentration values obtained in 13 wells before (i.e. non-purge method) and after purge (low-flow purge). No significant differences in concentration values were observed between the two sampling methods. Figure 2 shows the correlation between the concentration values obtained for the two methods. The linear regression displays a strongly significant ($R^2=0.982$) relationship with a slope coefficient of one between the two methodologies used during groundwater sampling. Additionally, stabilisation of thirteen wells during purging was monitored in the field (data not shown). It was observed that field parameters (pH, electric conductivity, dissolved oxygen, turbidity and temperature) were stable after purging approximately one bore volume (0.9 in average). These results suggest that the recommendation of purging 3 to 4 bore volumes is excessive in the case of aquifers contained in non-porous soils, which is the case of the site tested in this study.

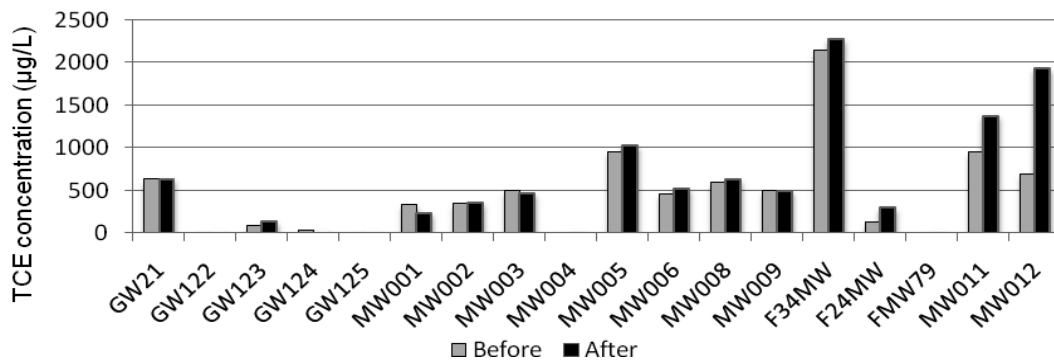


Fig. 1. Before and after purge TCE concentration

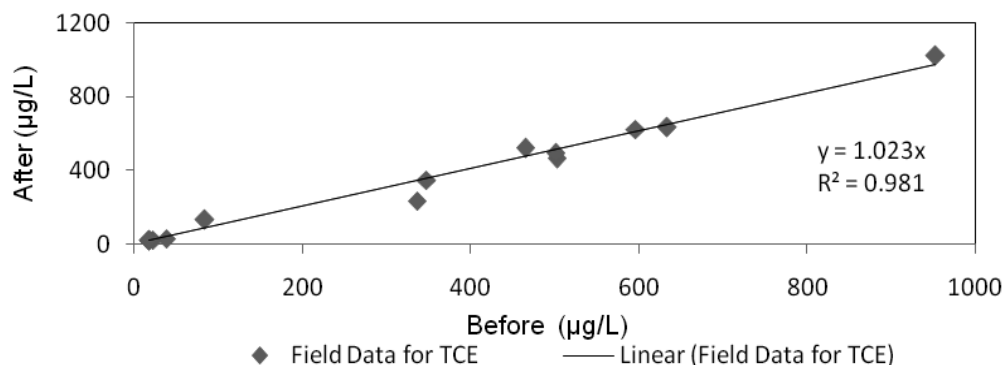


Fig. 2. Correlation between before and after values

CONCLUSIONS

No significant differences in concentration values between the sampling methods (low flow purge and non-purge) were observed for the site conditions tested (non-porous soil). Field parameters monitored during purge indicated that only one pore bore volume is required to achieve stabilisation. Further investigations are continuing at sites from varying geologic settings.

REFERENCES

- United States Environmental Protection Agency (1986) *RCRA ground-water monitoring technical enforcement guidance document*; EPA/530/SW-86/055; USEPA Office of Solid Waste and Emergency Response, 329p.
- Varljen, M.D., Barcelona, M.J., Obereiner, J., Kaminski, D. (2006) Numerical simulations to assess the monitoring zone achieved during low-flow purging and sampling. *Ground Water Monitoring & Remediation* 26: 44–52

APPLYING NUMERICAL METHODS TO IMPROVE LOW FLOW SAMPLING TECHNIQUE

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INTRODUCTION

Low flow sampling techniques are used to collect samples representative of the groundwater in the formation immediately surrounding the well screen without excessive purging. Such techniques have been endorsed by environmental agencies in recent years (Victoria EPA, 2000). Low flow sampling techniques are based on the maintenance of laminar groundwater flow in parallel layers with little mixing between layers. This can be achieved by drawing groundwater at a low flow rate, typically below 0.5 L/min. The techniques cause a stabilised low drawdown of the water level in the well. However, the appropriateness of low flow sampling techniques in various water bearing formations and under different sampling conditions is uncertain. There is a common misconception that low flow sampling techniques would draw water from the formation to the pump intake in parallel flow within a narrow horizon, thus the stagnant water in the well and in the filter pack would not be disturbed. It is also commonly understood that if a water bearing formation has a low hydraulic conductivity, this would not sustain a stabilised low drawdown and thus the low flow sampling techniques would not be applicable. This paper explores the uncertainties and assesses the applicability of low flow sampling techniques for various water bearing formations and under different sampling conditions.

METHODS

This work used established analytical relationships based on Darcy's Law, supplemented by the finite element numerical modelling software SEEP/W, to assess macroscopic flow characteristics and relationships between sampling conditions and groundwater flow for a hypothetical monitoring well. Various combinations of hydraulic conductivity conditions (representing various soil types) and sampling flow rates were assessed for potential influence on groundwater flow regime and drawdown in the well. The modelled geometry for each combination using the SEEP/W modelling package comprised a 5 m thick water bearing formation extending over a radius of 10 m in an axisymmetric setting, with a 5 m constant head applied at the far-field vertical boundary. The centre of the modelled geometry consisted of a typical monitoring well screened 2 m into the water bearing formation from the top. The screen was 0.05 m in diameter, surrounded by a sand filter pack of 0.16 m in diameter with a hydraulic conductivity of 1×10^{-4} m/s. A pump intake point was set 1 m below the top of the water bearing formation.

RESULTS AND DISCUSSION

To assess if low flow sampling techniques can be applicable, one common criterion used is the maintenance of low drawdown (dh) in the well (typically under 0.1 m), with the pump flow rate (Q) varying depending on the formation. Table 1 shows a set of conditions (Scenarios 1 to 5) that allow maintenance of drawdown within 0.1 m based on established analytical relationships. As per Scenario 5, low flow techniques, in theory, may still be applicable in a low hydraulic conductivity (k) formation (such as clays), as long as the water bearing formation has a sufficient thickness (L) for water to transmit.

The flow characteristics of selected k and Q combinations were further assessed using SEEP/W. Outputs from the SEEP/W modelling including head contours and flow paths were assessed. The results demonstrated that water generally did not flow to the pump intake in

parallel within a narrow horizon in a steady state condition. Water from the formation entered the well via the entire length of the filter pack prior to reaching the pump intake. Disturbance of the stagnant water in the well was evident. A SEEP/W output of head contours and flow paths for Scenario 2 is presented in Figure 1 for illustration purposes. Figure 1 shows that water entering the well from the entire length of the filter pack including an upward flow into the bottom of the well.

Table 1. Examples of scenarios (1 to 5) where drawdown (dh) can be maintained within 0.1 m.

Scenario	L (m)	Q (L/min)	k (m/s)	dh (m)	Examples of material
1	50	0.5	1×10^{-6}	0.1	silt, fractured rocks
2	5	0.5	1×10^{-5}	0.1	sand, permeable basalts, karst limestone
3	1	0.1	1×10^{-5}	0.1	sand, permeable basalts, karst limestone
4	10	0.1	1×10^{-6}	0.1	sand, permeable basalts, karst limestone
5	100	0.1	1×10^{-7}	0.1	fissured/weathered clays

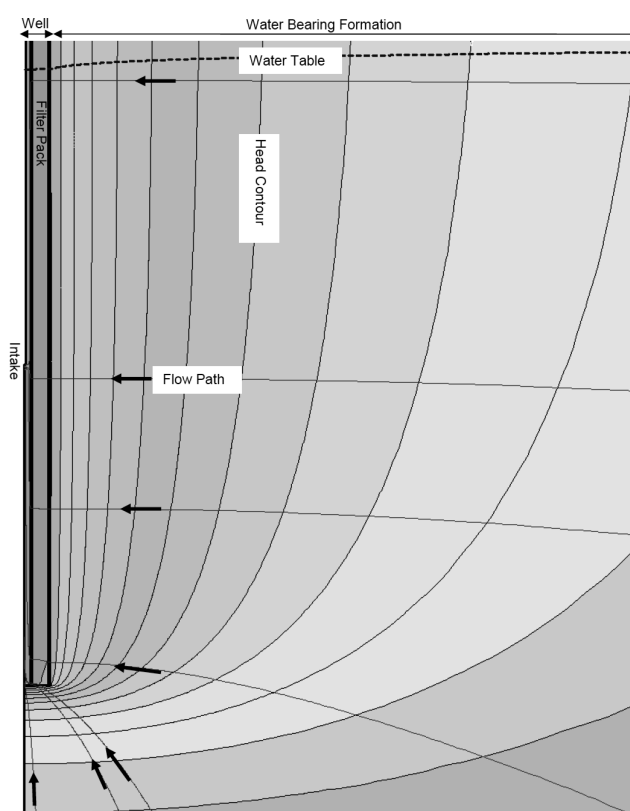


Fig. 1. Seep/W output for Scenario 2 showing a snapshot of head contours and flow paths.

CONCLUSIONS

The applicability of low flow sampling techniques is dependent on characteristics of water bearing formations and sampling conditions. SEEP/W results demonstrate that water does not generally flow in parallel within a narrow horizon to the pump intake. Water from the formation enters the well via the entire length of the filter pack prior to reaching the pump intake. Analytical methods and numerical modelling can assist in further research on the applicability and limitations of low flow sampling techniques to obtain representative groundwater samples from the surrounding formations.

REFERENCES

Victorian EPA (2000). Groundwater Sampling Guidelines, Publication 669, Victorian EPA, Southbank, Victoria, Australia.

CONTAMINATION ASSESSMENT OF A FUEL PIPELINE IN NSW – THE CHALLENGE OF MULTIPLE SOURCES OF CONTAMINATION IN A HEAVY INDUSTRIAL AREA

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INTRODUCTION

An underground pipeline, owned by an oil & gas company, was formally used to transfer liquid fuels from a terminal site to a distribution depot in southern Sydney. The pipeline followed existing road corridors in the area, typically installed at approximately 0.5 metres depth beneath foot paths and nature strips. A neighbouring property used for the manufacture of industrial chemicals had previously constructed a waste landfill adjacent to a portion of the fuel pipeline for disposal of various chemical waste streams. The neighbouring owner alleged that potential releases of fuel from the pipeline may have caused the degradation of the synthetic liner used for the base of the landfill.

The oil & gas company was obliged to conduct a detailed assessment of the fuel pipeline and the surrounding soil and groundwater to establish whether the pipeline had caused contamination that may have impacted the integrity of the liner of the landfill. Although some groundwater contamination data were provided by the neighbouring site to assist in conducting the assessment, intrusive investigations or sampling on the neighbouring site could not be undertaken.

The site is located above an extensive unconfined sandy aquifer. The standing water level beneath the site was approximately 8 metres below ground level (mbgl).

METHODS

An initial desk top study was conducted to obtain relevant information on the contamination history of the area and the operational history of the pipeline. The results of the desk top review were used to develop a preliminary conceptual site model (CSM), which formed the basis of an intrusive investigation, including drilling and installation of six groundwater monitoring wells. Soil and groundwater samples were collected for analysis of potential chemicals of concern including petroleum hydrocarbon compounds associated with products transferred by the pipeline and chlorinated volatile organic compounds (VOCs), known to be present in the waste encapsulation. In addition, groundwater samples were submitted for key geochemical parameters, which were used for assessment of natural attenuation processes.

An additional phase of assessment included exposing the fuel pipeline in three locations to assess its condition and the condition of the surrounding soil. This was followed by a soil vapour assessment at the same three locations. Vapour samples were collected using thermal desorption tubes and were analysed for VOCs.

RESULTS AND DISCUSSION

The results of the desk top assessment indicated significant concentrations of chlorinated VOCs and benzene, toluene, ethylbenzene and xylene (BTEX) in groundwater in the vicinity of the pipeline and the neighbouring property. The results of the soil assessment indicated little to no contamination in the vadose zone, with BTEX and VOC contamination evident at 8 mbgl at the approximate depth of the water table. The groundwater assessment revealed significant BTEX and VOC contamination, consistent with the results from the desk top study

and the soil assessment. The geochemical parameters showed evidence of natural attenuation with oxygen, nitrate and sulphate depletion and the presence of ferrous iron, manganese and methane in the impacted areas indicating the consumption of electron acceptors. Conversely, in monitoring wells located away from the impacted area, oxygen, nitrate and sulphate levels were elevated and ferrous iron, manganese and methane concentrations were lower or not detected.

The results of the soil vapour assessment showed little to no evidence of BTEX vapours in the upper 2 metres of the soil profile, but did show distinct evidence of chlorinated VOCs.

CONCLUSIONS

The assessment concluded that there was no evidence of any releases of fuel products from the pipeline, supported by the lack of petroleum hydrocarbon contamination in soil and vapour at shallow depth. The presence of chlorinated VOCs in groundwater and vapour was attributed to the neighbouring waste encapsulation.

It was therefore considered unlikely that the fuel pipeline was the cause of the BTEX contamination. In addition, based on the vapour results, it was also unlikely that the BTEX contamination was the cause of any potential failures to the liner of the waste encapsulation.

Following review of the assessments by the NSW Department of Environment, Climate Change and Water (DECCW), it was agreed that sufficient evidence was provided demonstrating that the oil & gas company was not responsible for the impacts to groundwater from leaks of the former fuel pipeline.

A key outcome of this assessment was the difficulty of conducting contamination assessments in isolation of all available information. Due to the focussed nature of the assessment, it was not possible to update the CSM for the site. The areas surrounding the pipeline have been used for industrial purposes over a prolonged period and potential sources of contamination from up-gradient sites cannot be excluded. A holistic approach to assessing the contamination in this area over various property boundaries and involving multiple parties would be required to fully resolve the issue.

REFERENCES

- GHD (2009a) *Former Pipeline Corridor between Wight Street and Corish Circle, Banksmeadow: Environmental Review*. Report reference: 21/18709/152025. 1 October 2009.
- GHD (2009b) *Botany Bay Pipeline: Additional Groundwater Assessment*. Report reference: 21/18709/154787. 26 October 2009.
- GHD (2010) *Report for Corish Circle Fuel Pipelines: Environmental Site Assessment and Subsurface Pipeline Inspection*. Report reference: 21/18709/157514. May 2010.
- URS (2008) *Risk-Based Remediation Concentrations: Car Park Waste Encapsulation*. Report reference: 43217564. 28 November 2008.

A NEW METHOD FOR ASSESSING ACID NEUTRALISING CAPACITY IN ACID SULFATE SOIL MATERIALS

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INTRODUCTION

Acid Base Accounting (ABA) is the industry accepted method to determine the acidity hazard of acid sulfate soil materials (Ahern, McElnea and Sullivan (2004). The current ABA is:

Net acidity = potential sulfidic acidity + existing acidity – acid neutralising capacity

Methods for assessment of both the potential sulfidic acidity are well accepted and for existing acidity are under development (see Vithana et al.'s paper in these proceedings) However, current methods for the assessment of acid neutralising capacity (ANC) are not well accepted by industry and regulators. Indeed when using standard Acid Base Accounting (ABA) methods to determine the acidification hazard of these materials, the ANC term of the ABA is often ignored by regulators due to the known deficiencies of the existing ANC methods. This is an important issue as it can lead to costly false positive hazard identification occurring in development sites in turn can lead to costly liming practices being used when not required.

The development of more appropriate and accurate ANC methods have been constrained by a lack of knowledge of the effectiveness of acid neutralising components in soils and sediments. Current ANC assessment approaches use either back titration methods or direct carbonate determinations to measure ANC. Both of these methods are open to criticism as they are both subject to over-estimation due to interferences. For example, the strong acids used in the back titration methods lead to digestion pHs $\ll 1$ and thus have included unacceptable neutralisation processes (as accepted in the acid sulfate soil scientific community but not the acid rock drainage scientific community) such as aluminosilicate dissolution. Such processes as considered unacceptable in acid sulfate soils as they lead directly to contamination via e.g. production of potentially-toxic soluble aluminium.

One of the main aims of our CRC CARE project has been to overcome the deficiency in existing ANC methods and provide industry with a suitable and far more accurate and reliable method for ANC determination in acid sulfate soil materials. The new ANC assessment method is as below:

ANC = TAAIk + Effective Carbonate

Titrateable Actual Alkalinity (TAAIk)

The readily available acidity of acid sulfate soil materials (due to soluble and exchangeable acidity fractions) has long been determined by the measurement of the Titrateable Actual Acidity (TAA) and included in the ABA. However the contrary measure i.e. readily available alkalinity of acid sulfate soil materials has never previously been measured separately. (It has been included within the ANC measure provided by the back titration methods but as discussed previously these back titration methods are largely discredited within the industry). Titration curves of a range of acid sulfate soils from NSW, Qld, SA, and WA have demonstrated that a measure of TAAIk is warranted, can be substantial, and can be easily measured using existing acid sulfate soil analytical approaches.

Whereas TAA is the acidity released by acidic soil materials to a 4M KCl solution and determined by titration with NaOH up to a pH of 6.5, TAA_{alk} is simply the alkalinity released by alkaline soil materials to a 4M KCl solution and determined by titration with HCl down to a pH of 6.5. Importantly this new ANC method is very suitable for direct incorporation in the industry-accepted Laboratory Method Guidelines (including Acid Base Account model) for acid sulfate soil materials of Ahern, McElnea and Sullivan (2004).

Effective Carbonate (eCarb)

The appropriate particle size range of carbonate liming materials that can effectively neutralise either 1) the existing acidity or 2) the potential acidity production within acid sulfate soils has – prior to this project - never been determined. Prior to this project, shell materials <2 mm in size have been accepted as being effective for acid neutralization in acid sulfate soils (e.g. Ahern, McElnea and Sullivan, 2004). Prior to this project the effectiveness of agricultural (i.e. geological) lime materials have been accepted (on the basis of particle size) as: <0.300 mm are 100% effective; between 0.300 mm to 0.850 mm are 60% effective, and; >0.850 are 0.10% effective. These assumptions on the effectiveness lime particle sizes have little basis: accordingly, managers use these assumptions with less-than-full confidence.

METHODS

Incubation/remediation trials using representative acid sulfate soil materials and nine particle size fractions of liming materials (i.e. < 0.020 mm up to 1.0 mm-2.0 mm) were used to provide the first data on liming efficacy in acid sulfate soil materials in relation to the particle size of liming agents, and form the basis of the Effective Carbonate determination method.

RESULTS

These results clearly show that for effectiveness of prevention of acidification:

- in neutral or alkaline sulfidic material that is subject to oxidation, liming materials need to be <0.5 mm in size to be effective in avoiding acidification,
- in acidic acid sulfate soil material that has already been subject to oxidation, liming materials need to be <0.25 mm to be effective in remediating soil pH within 2 weeks and <0.5 mm to be effective in remediating soil pH within 4 weeks.

A simple method for the determination of Effective Carbonate content follows these results:

Effective Carbonate content is the carbonate content (as determined by standard carbonate analytical techniques) of the <0.5 mm size fraction of unground soil material.

CONCLUSIONS

The new assessment procedures outlined here has shown the way forward to develop accurate and reliable determinations of ANC in acid sulfate soil materials. This will allow ANC to be accounted for in determining the acidity hazard of acid sulfate soil materials with confidence.

REFERENCES

Ahern, C.R., McElnea, A.E. & Sullivan, L.A. (2004) Laboratory Methods Guidelines 2004- Acid Sulfate Soils. In *Queensland Acid Sulfate Soil Technical Manual*. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

UNDERESTIMATION OF RETAINED ACIDITY MEASURED USING THE NET ACID SOLUBLE SULFUR (S_{NAS}) METHOD IN ACID SULFATE SOILS CONTAINING SCHWERTMANNITE AND JAROSITE

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INTRODUCTION

Retained Acidity (RA) is one of the components of Acid Base Account (ABA: Equation 1 & 2) which is an approach widely used in the world in managing the Acid Sulfate Soils (ASS) (Ahern *et al.* 2004). Two major contributors of RA are thought to be jarosite and schwertmannite which are relatively insoluble ironhydroxysulfate minerals but release acidity in the long run as they weather by hydrolysis (Ahern *et al.* 2004; Burton *et al.* 2007).

$$\text{ABA} = (\text{Potential Sulfidic Acidity} + \text{Existing Acidity}) - \text{Acid Neutralization Capacity} \quad (1)$$

$$\text{Existing Acidity} = \text{Actual Acidity} + \text{Retained Acidity} \quad (2)$$

One of the main methods used to assess the RA fraction in ASS in Australian laboratories is the Net Acid Soluble Sulfur (S_{NAS}) method (Ahern *et al.* 2004). This study was aimed to determine for the first time the actual contribution of schwertmannite to S_{NAS} determinations in ASS and assess systematically the ability of the S_{NAS} method to quantify schwertmannite and jarosite content in ASS materials.

METHODS

Synthetic schwertmannite and jarosite were spiked from 0.125%-5% in non-acid sulfate soils samples collected from Richmond and Clarence River catchments in north-eastern NSW, Australia and analysed for S_{NAS} . Quartz was used as the reference. For S_{NAS} , two separate soils samples were analysed for 4M HCl extractable sulfur (S_{HCl}) and for 1M KCl extractable sulfur (S_{KCl}). S_{NAS} was determined as shown in the Equation 3.

$$S_{NAS} (\%) = S_{HCl} (\%) - S_{KCl} (\%) \quad (3)$$

For the S_{KCl} determination, the sample was extracted with 1M KCl for 4 hrs followed by a titration with 0.05M NaOH to pH 6.5 if the pH of the 1M KCl extract was < 4.5. The acidity determined by titration is a measure of Actual Acidity (AA) which is denoted as Titratable Actual Acidity (TAA). S_{HCl} (%) fraction was determined by extracting the spiked sample with 4M HCl for 16 hrs.

RESULTS AND DISCUSSION

Synthetic schwertmannite added samples released acidity and sulfate during 1M KCl extraction in line with the increase of added schwertmannite content in the sample. Approximately 1/3 of the expected inherent acidity was released during 1M KCl extraction from schwertmannite and was measured as TAA. This observation was shown irrespective of the presence of the soil/quartz matrix. The release of sulfate during KCl extraction can be explained as the release/exchange of sulfate bound to the surface of schwertmannite. According to Bigham *et al.* (1990) and Jönsson *et al.* (2005) ~30 % of sulfate in schwertmannite is bound to the surface and hence can be exchanged or released at higher

pH (> 6.5). As expected there was zero or very little generation of AA or KCl soluble sulfate in synthetic jarosite added samples.

S_{NAS} was not able to reliably measure the content of synthetic schwertmannite added to ASS samples (Figure 1a). On the contrary, the S_{NAS} calculated for synthetic jarosite was more than half of the expected sulfur (Figure 1b).

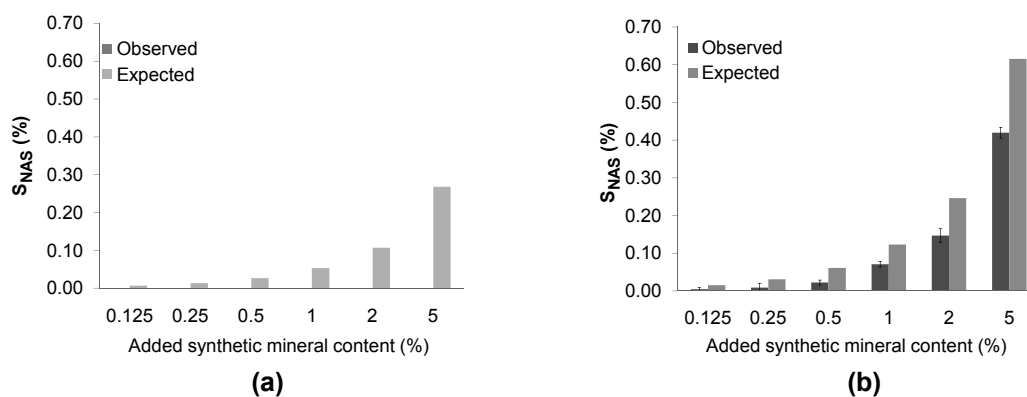


Fig. 1. S_{NAS} (%) a) synthetic schwertmannite b) synthetic jarosite added Clarence soil samples

CONCLUSIONS

Schwertmannite releases acidity and sulfate during 1M KCl extraction which is measured as AA and KCl soluble sulfate. As a result, the RA fraction that is determined from S_{NAS} was unreliable for the quantification of schwertmannite in ASS samples.

For jarosite added samples, S_{NAS} slightly underestimates the RA fraction but can be used to estimate jarosite content reliably with suitable factors included to account for incomplete jarosite recovery.

Further research is being undertaken to examine whether the synthetic schwertmannite and jarosite minerals examined here behave similarly to naturally occurring minerals.

REFERENCES

Ahern, C.R., McElnea, A.E. and Sullivan, L.A. (2004) Acid Sulfate Soil Laboratory Methods Guidelines, Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Bigham, J.M., Schwertmann U., Carlson, L. and Murad, E. (1990) A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. *Geochim. Cosmochim. Acta* .54: 2743-2758.

Burton, E.D., Bush, R.T., Sullivan, L.A. and Mitchell, D.R.G. (2007) Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands. *Geochim. Cosmochim. Acta*. 71: 4456-4473.

Jönsson, J., Persson, P., Sjöberg, S. and Lövgren, L. (2005) Schwertmannite precipitated from acid mine drainage: phase transformation, sulphate release and surface properties. *Appl. Geochem.* 20: 179-191.

THE DANGERS OF USING ICE IN SAMPLE ESKIES

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INTRODUCTION

Laboratory results can only be considered as good as the samples supplied. If during the sampling or transportation process integrity has been compromised, then results should possibly be treated as questionable. This report will briefly outline one of the practices in common use by environmental consultants that some may consider to produce questionable data.

ICE IN ESKIES

Using ice to cool and transport samples to the laboratory is a common technique, however, it can potentially result in cross contamination. Ice tends to melt rapidly and it is not uncommon for samples to then be received in the laboratory swimming in a pool of muddy ice water. Though most sample jars and bottles seal well, there are occasions when grit in a jar thread will prevent a lid from sealing properly. In these cases it is likely that melted ice water will make contact with the sample.

Several references give sensible recommendations about using ice:

“All sample containers should then immediately be placed in a plastic bag in a cooler/esky below 4°C, taking care to ensure that melted ice does not cause the sample containers to become submerged” (NSW EPA, 1994).

“It is best not to use ice in the cooler in case water from the melting ice contaminates the sample” (NSW Department of Primary Industries, 2003).

The current NEPM (NEPC, 1999) tends to give broad advice –

“.....store vials and jars on ice, or in a refrigerator at 4°C, for transport to the laboratory”, while the new Draft NEPM (NEPC, 2010) is moving in the right direction by excluding the word ice -

“...transported under suitable cooling aids (for example, ice bricks, refrigerated container) to ensure sample starts cooling as soon as possible....”

As the NEPM provides a national approach to contaminated sites, it could be argued, based on the results below in Table 1, that stronger wording could be used with the NEPM banning the use of ice altogether, unless there is an additional barrier between ice and samples.

RESULTS AND DISCUSSION

Over a period of two weeks in January/February 2011, melted esky ice water was collected on receipt at the laboratory into nitric acid preserved bottles. It was then digested, and analysed by ICP-MS for total recoverable metals. One sample also underwent microbiological analysis for Total Coliforms.

The results are summarised in Table 1 below. Eskies were received from various sites in NSW by various environmental consultants. To maintain anonymity consultants and specific sites have not been recorded. Only melted ice that was visibly compromised (muddy) was sampled. The contaminated ice water was therefore the result of either broken soil jars, leaking soil jars, mud from the outside of soil jars or loose soil present in the esky. As can be seen, a variety of heavy metals have been detected. The significant concentrations could potentially contaminate samples where container integrity has been compromised. Note that the laboratory detection limit for most elements is 1µg/L (ppb).

**Table 1. Contaminants detected in Esky Ice
(Metals in µg/L (ppb), Microbiological in CFU/100ml)**

	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H	Site I
Al	200	140	50,000	2,700	22,000	1,300	5,800	200,000	41,000
As	2	1	58	2	20	2	2	35	9
Cd	0.3	0.1	2	7	0.9	<0.1	0.2	7	1
Co	<1	<1	49	4	28	5	1	930	49
Cr	2	5	56	6	44	1	6	120	99
Cu	12	12	730	16	65	18	14	3,700	180
Fe	360	380	51,000	6,400	24,000	1,500	7,500	600,000	59,000
Pb	3	3	130	9	49	1	35	120	120
Mn	45	14	1,200	130	540	130	56	56,000	2,800
Ni	3	2	26	5	28	3	2	450	140
Se	2	2	3	1	2	<1	<1	3	2
Zn	41	31	900	86	350	23	77	660	1,800
Sb	22	7	5	2	2	1	<1	<1	<1
Ba	7	12	630	76	210	10	120	1,900	1,100
Be	<1	<1	4	<1	2	<1	<1	47	5
B	28	19	110	16	38	25	17	67	74
Mo	4	<1	6	<1	2	6	<1	4	2
Tl	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sn	5	2	30	8	8	1	18	1	2
V	3	<1	200	10	65	4	11	1,400	160
Th	<1	<1	24	1	8	<1	3	120	20
U	<1	<1	17	<1	1	<1	<1	24	5
Micro									18,000

CONCLUSIONS

To avoid potential sample contamination Envirolab recommends the use of ice only to initially chill samples and the use of ice bricks (or ice in sturdy plastic bags) during transportation.

REFERENCES

- NEPC (1999) B3, National Environment Protection (Assessment of Site Contamination) Measure – Guideline of Laboratory Analysis of Potentially Contaminated Soils. pp.33
- NEPC (2010) B3, Draft National Environment Protection (Assessment of Site Contamination) Measure – Guideline of Laboratory Analysis of Potentially Contaminated Soils. pp.19
- NSW EPA (1994) Guidelines for Assessing Service Station Sites. Appendix B.
- NSW Department of Primary Industries (2003) Successful Silage. pp314.

VULNERABILITY OF INDOOR AIR TO AIRBORNE THREATS RELEASED INSIDE A BUILDING

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INTRODUCTION

In this study, we have conducted extensive computational fluid dynamics (CFD) simulations and tracer gas dispersion experiments to characterize the dispersion of toxic gases released at two of Perth's iconic buildings: (i) Fremantle Passenger Terminal and (ii) Perth Underground Train Station.

METHODS

Four tracer gas experiments were conducted at the Fremantle Passenger Terminal (FPT), and six different scenarios were investigated using CFD modeling. A comparative analysis of experimental observations and CFD simulations found that the geometrical structures inside the building, e.g. temporary partitioning for guidance through the Customs area, played a significant role in the dispersion of the tracer gas. Six tracer gas experiments were performed at the Perth Underground Train Station (PUTS) from June 2009 to February 2010.

RESULTS AND DISCUSSION

In most of the case studies at the FPT, the peak concentration inside the supervisor's office was lower by five orders of magnitude than the region outside the room. Under the circumstances investigated in this study, the supervisor's room could be considered a safe haven, in the event of a terrorism-related release of a toxic gas, provided the release point of the gas was up or down wind from the room. However, if the release point was near the office door, then a significant amount of tracer was shown to enter and remain in the office, because of the lack of ventilation (Figure 1).

Since FPT is situated on the coast, there were significant fluctuations in the wind speed and direction which created some uncertainties in correctly simulating the flow inside this building. It was also observed that the flow from the entry door in the FPT had a large influence on the tracer dispersion pattern. Original test conditions had the passengers entering the terminal from a side door, facing the ocean. The CFD simulations suggest that this arrangement was not ideal when considering the movement of a toxic gas within FPT. The 90° ventilation configuration created vortices inside FPT, thus trapping the tracer gas, rather than removing or clearing it.

The tracer gas experiments and modeling results concluded that the tracer gas at the PUTS dispersed more rapidly, and was influenced by both environmental conditions and from the movement of trains throughout the underground area. Geometrical structures inside the building e.g. escalators and pillars located on the platform, also played a significant role in the dispersion of the tracer gas. Experimental and modeling results complemented each other, with the near plug flow conditions producing negligible back-mixing of the tracer gas. This led to formation of a region upwind from the release point with low concentrations of tracer gas, which could be considered a potential safe haven for people on the platform.

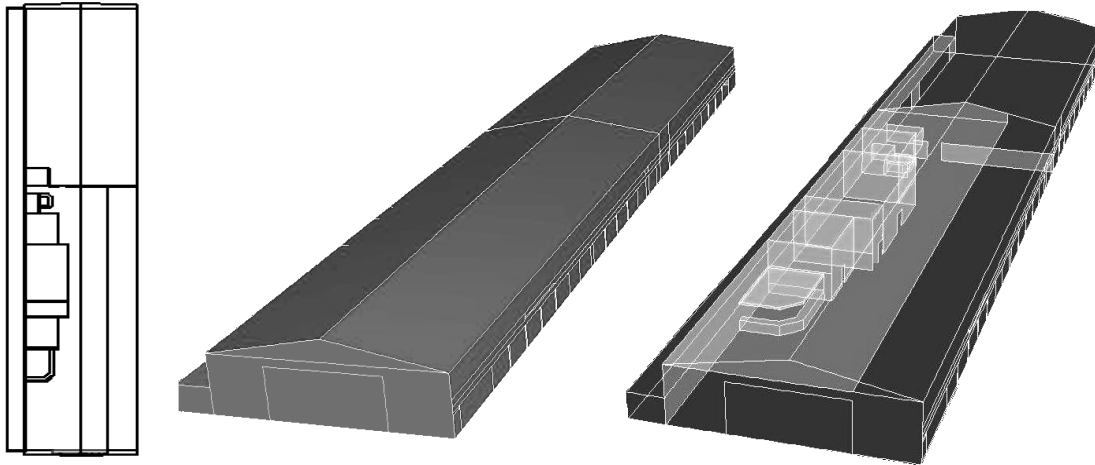


Figure 1. Floor plan of PUTS.

CFD predictions for the dispersion of tracer gas inside PUTS matched well with the experimental data; however, a relatively poor comparison was achieved for the FPT, possibly due to the discrepancies associated with wind speed/direction from sudden gusts. Since CFD simulations were conducted at constant wind speed, these sudden and momentary changes in the wind speed led to errors in CFD predictions. At the PUTS wind conditions were mostly steady with only changes occurring because of the arrival and departure of trains. Both CFD and experimental tracer gas studies found the best areas to shelter or evacuate to be those upwind of the release point for both FPT and PUTS.

CONCLUSIONS

CFD predictions and experimental observations using tracer gas for four different case studies were compared with each other. While CFD predictions for the dispersion of tracer gas inside the Perth Underground Train Station (PUTS) matched well with the experimental data, a relatively poor comparison was achieved for the Fremantle Passenger Terminal (FPT). The CFD simulations were performed at constant wind speeds and sudden momentary changes in the wind speed were not able to be captured, leading to discrepancies between experimental results and simulation predictions. A benefit of using the tracer gas experimental approach is that it is able to capture and resolve changes on gas concentration, as a result of fluctuations in wind conditions.

Experiments at the PUTS yielded similar results, with the wind conditions being affected by the arrival and departure of trains onto the platform. The train movements into the PUTS were able to be captured in the experimental results however was not able to be seen in the predicted CFD simulations. Other than fluctuations in the movement of air caused by the trains, the results at the PUTS were consistent with the CFD predictions, as the overall wind speed within the PUTS was steady.

Both the experimental and CFD results confirm the movement of people upwind from a release of toxic material will minimise their exposure to a chemical.

ACKNOWLEDGMENT

The researchers acknowledge the financial support from the CRC-CARE and NSST (National Security Science and Technology Branch of Federal Government of Australia). The research team also expresses its sincere gratitude for staff at Fremantle Passenger Terminal (FPT) and Perth Underground Train Station (PUTS), most notably for Mr David Brown, Mr Michael Jordon and Mr Robert Whettters of PUTS, and Mr Ray of FPT. Our thanks also due to Mr Leith Higgins (FESA) for liaising with both FPT and PUTS for carrying out this study. Finally, we also thank over a 2 dozen volunteers from both Chem Centre and Curtin for actively participating in collecting samples of the tracers gas.

GROUNDWATER ANALYSIS: MINIMIZING FALSE POSITIVES AND NEGATIVES – A KEY STEP IN EFFECTIVE GROUNDWATER REMEDIATION

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BACKGROUND

Groundwater sampling has evolved significantly over the last decade with many changes in practices including an increase in the use of low flow pumps. Field filtration in the nineties was often difficult, risks of field contamination were higher and guidance on field preparation was in many cases inconsistent across laboratories. From a laboratory perspective, the average Amber glass bottle in the late nineties submitted for PAHs, TPH or Semi-volatile organics often contained significant amounts of sediment up >50,000mg/L. Today, most ground waters submitted have significantly less sediment. What have these changes meant from a quality and data perspective and how can data quality be optimised?

SEMI-VOLATILE ORGANICS

A decade ago, many groundwater samples included percentage levels of sediment. The greatest impact on results was often simply down to the way in which laboratories processed the samples. Options known to be used included – decant off the water and ignore the sediment, shake the bottle and take all of the sediment, take the entire contents of the bottle and solvent rinse the container, decant the water, tip out the sediment then solvent rinse the container. Each of these had significant implications on the results for some parameters and impacts on data accuracy will be discussed using some case studies.

Further discussion will reference EPA guidance on sampling and where we are at ten years later in the search for high quality, reproducible data. Progressions in laboratory practices that impact sample collection will also be discussed as well as presentation of some new sampling and analysis options that may provide the environmental industry with tools to further evaluate semi-volatile organics in groundwater.

FIELD FILTRATION - METALS

Field filtration of metals is also a topic with many opinions. This presentation will discuss changes over the last decade in the samples generally received by a laboratory. It will also highlight some easy ways (and real examples) of how to get very wrong results and look at where the industry is at 10 years on from a sampling and laboratory data quality perspective.

SAMPLING GROUNDWATER – NEW TECHNIQUES BEING TRIALLED IN THE US

This portion of the presentation will discuss some of the latest techniques being used in the US which may present efficiency, quality and sustainability benefits and how the laboratory plays a key part in facilitating these new approaches.

CONCLUSION

While sample quality has improved greatly over the last decade, differing field techniques still risk false positives and negatives for some parameters. Education on key risks and sharing of appropriate practice should lead to improved data quality and benefit decision making on the whole.

CAUSES AND EFFECTS OF RANDOM VARIANCE IN SPATIAL DATA SETS AND EFFECTS ON RELIABILITY OF CONTAMINATION DISTRIBUTION INTERPRETATION

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INTRODUCTION

Application of linear spatial geostatistical methods to contaminated sites data offers a powerful and informative alternative method of interpreting contaminated site assessment concentration data to the traditional hot spot uni-variate statistically based approach utilised in Australian practice. Unlike to hot spot approach the spatial geostatistical method does not require the assumption of a specific size and shaped target of uniform contamination assessed using an unbiased systematic sample location approach to establish presence or absence at a desired confidence level.

BACKGROUND AND APPROACH

Use of linear spatial geostatistics (Lognormal-de Wijsian approach) developed by Krige allows evaluation of spatial relationships on variance and separates the spatial and random components through use of variograms. This approach overcomes the limitations and assumptions of the hot spot approaches and provides a powerful tool to assess the adequacy and uncertainty associated with site characterization data. Indicator Kriging allows for probability based delineation of clean and impacted areas on a site.

One of the common issues encountered in application of linear spatial geostatistics is how to account for random variance at the micro and macro scale when using concentration data generated using routine sampling and analysis methods. The variogram generated from the sample coordinate and concentration data (example on Figure 1) splits the total data set variance into a random and spatial component and established the range of influence (distance) over which any spatial variance component applies.

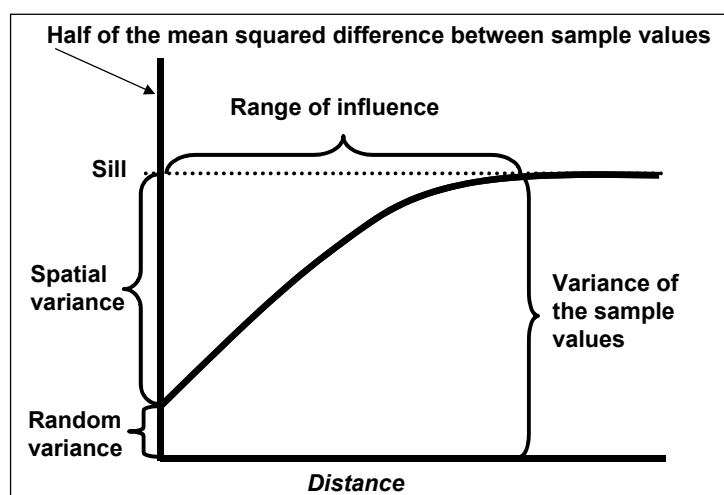


Fig. 1. Properties of the variogram.

The random variance component is comprised of two elements, the non spatial component of variance between sample locations (macro component) and the sample scale component (micro component). In data sets with a very strong spatial variance component, use of the

primary concentration data may lead to an overestimation of the confidence at which the impacted and un-impacted zones of the site are defined as this ignores any potential effects of the micro scale variance.

Guidance requires the collection of blind duplicate and split samples to assess accuracy and precision of analysis. In many situations non compliance with acceptance criteria for these Data Quality Indicators (DQI) is attributed to sample heterogeneity, which when dealing with heterogenous geological materials is often a valid argument. Yet when this DQI data is gathered, little more is done with it outside of the quality checking. However this data provides a valuable insight into the impact heterogeneity can have on overall data variance. Also this data can be utilised in linear spatial geostatistical assessment to incorporate micro scale random variance into the method.

The effect of micro scale random variance was assessed using a 303 primary sample data set for priority metals collected from a 2ha site and nearby surrounds proposed for residential use in western Melbourne. Guidance values were exceeded for one or more contaminants of concern in up to 108 samples (36%). For the purpose of this analysis lead was chosen as the contaminant for assessment. Developing two input data sets, one with the primary sample data only and one with primary, duplicate and split sample concentrations included. Comparison of the variograms for untransformed data show the effects that inclusion of the duplicates had on the distribution of variance between the spatial and random components, as shown on Figure 2. As shown the random variance component increases once the duplicate and split samples are included, increasing from <1% to ~10%. This then affects the confidence plots developed from indicator kriging as the maximum confidence achievable decreases from nearly 99% to around 90%.

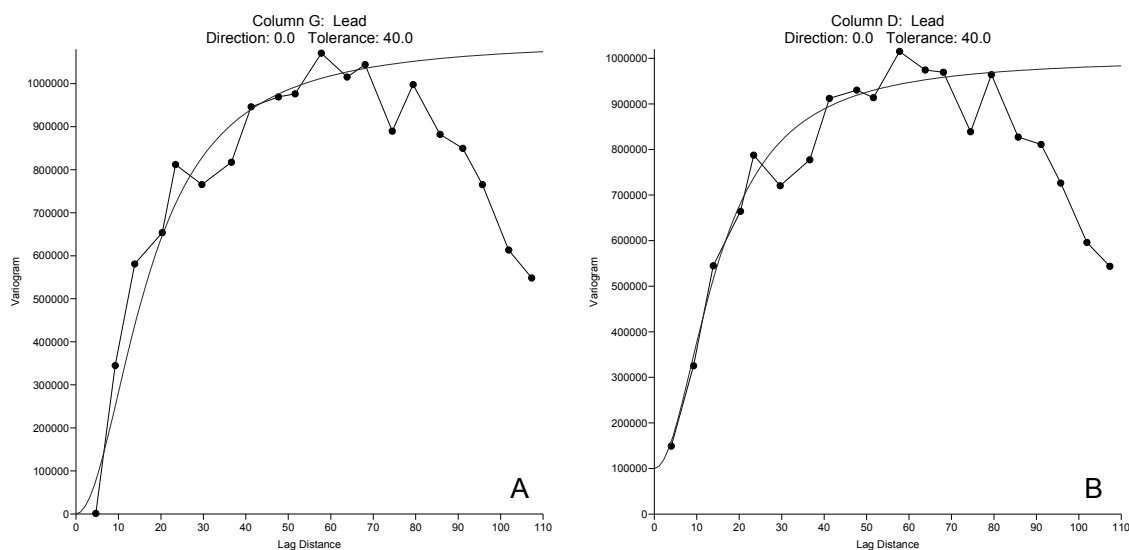


Fig. 2. Variograms for lead data, A – primary samples only, B – primary, duplicate and split samples.

CONCLUSIONS

This study has demonstrated that the inclusion of duplicate and split samples with the primary sample concentration data can allow for inclusion of micro scale variance that allows for more realistic simulation of the random and spatial variance components. Application of this approach to a lead data set has demonstrated that inclusion of the micro scale variance resulting in an increased random variance component of the variogram and associated model. This then affects the confidence limits at which contaminant presence or absence can be mapped on sites. In the case of the lead data set utilised the random variance component increased from <1% to ~10% limiting the upper confidence limit that can be achieved to 90%.

CONTAMINATED SITE ASSESSMENTS – IT'S MORE THAN JUST NUMBERS

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INTRODUCTION

Over the past two decades, and particularly since the publication of the National Environment Protection (Assessment of Site Contamination) Measure 1999 (NEPC 1999), assessments and remediation of contaminated sites has often been driven by the need to achieving the NEPM health based investigation levels (HILs). While the HILs provide Australian industry and the community security that sites are “clean”, provided chemical concentrations are less than the HILs, pragmatic, scientifically justifiable evaluation of all site data often takes second place to “checking the numbers”. Information such as soil types, geology, aquifer characteristics and chemical attributes (as well as of course the chemical concentrations) should be considered together in developing conceptual site models so that the “true risk” of exposure to the chemicals that may be present on a site can be made. The following project demonstrates the importance in critically evaluating all data collected during an investigation or validation program rather than placing blind faith in the absolute numbers.

PROJECT

In 2008, GHD (GHD 2010) was engaged to conduct an investigation of a former coal mining lease. The property was to be handed back by the mining operators to the site owners, and as part of the hand over, the mining operators were obliged to evaluate the potential impacts from the former mining activities. The primary area of concern identified in the investigation was the presence of a diesel above ground storage tank (AST). The investigation revealed that spillages had occurred in and around the AST and that not only the soils in the immediate vicinity of the AST, but a significant distance down gradient, had been contaminated with hydrocarbons. The area down gradient of the AST comprised an unlined drainage channel. Subsequent sampling of the soil in and around the drainage channel revealed the presence of hydrocarbons in excess of the nominated investigation levels. The puzzling outcome of the initial data interpretation was that a number of the elevated hydrocarbon results were not associated with the drainage channel.

RESULTS AND DISCUSSION

Given that hydrocarbons were identified in soils that were not likely to form the drainage pathway, a reassessment of the existing data was performed to understand whether there was another hydrocarbon source present on site. This assessment centred on reviewing the chromatograms that had been generated for the collected samples.

The evaluation of the chromatograms showed there to be two distinct hydrocarbon signatures. A comparison of the logs of the soil samples and the chromatograms showed that the hydrocarbons in many of the samples collected outside the interpreted drainage flow path were in fact related to the presence of coal and not diesel. Figures 1 and 2 show the two different hydrocarbon signatures.

The ability to distinguish diesel contamination from the response to the laboratory analysis to the presence of coal in the samples was an important step in defining what further investigation and remedial works were required to address impacts to the site from spills from the AST, rather than continuing to assume that the elevated hydrocarbon concentrations were evidence of diesel contamination.

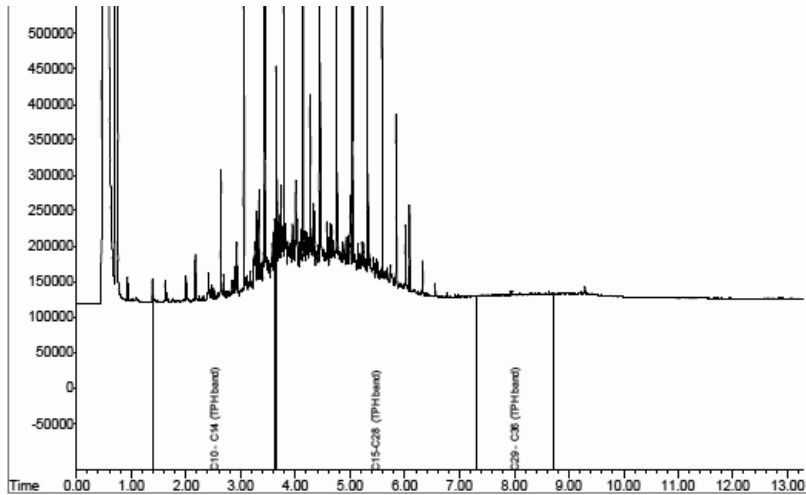


Figure 1. Diesel chromatogram.

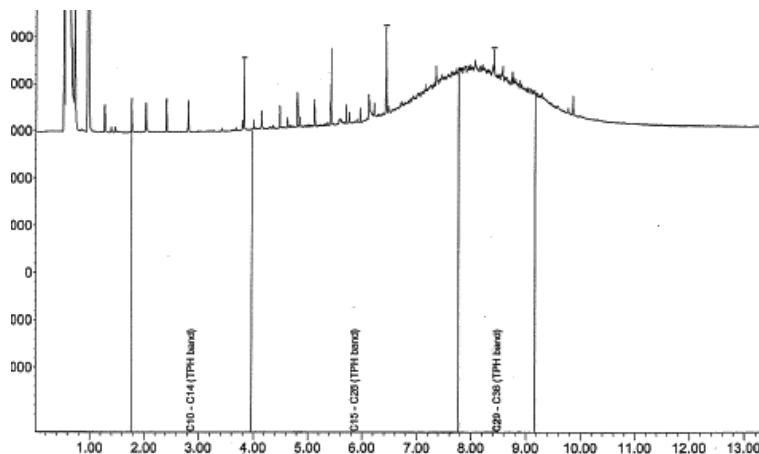


Figure 2. Coal chromatogram

CONCLUSIONS

The outcome of the evaluation of all site data allowed investigation and subsequent remedial works to only focus on the area where diesel contamination had occurred and avoided unnecessary remedial works. The study also demonstrated that conceptual site models and site investigations should consider all project data and that the numbers are a means to an end, not the end itself.

REFERENCES

- GHD (2010) *Stage One and Stage Two Contamination Assessments of the former EnhancePlace Mine.*
- National Environment Protection Council (1999) *National Environment Protection (Assessment of Contamination Sites) Measure 1999*

HIGH RESOLUTION SITE CHARACTERIZATION: AN INNOVATIVE APPROACH TO SITE INVESTIGATIONS TO SUPPORT EFFECTIVE DECISION MAKING

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INTRODUCTION

Site investigation programs, particularly in complex settings or on larger sites, often involve seemingly endless phases of assessment that result in development of low quality conceptual site models (CSMs), resulting in unreasonably high degrees of uncertainty. This uncertainty is primarily driven by sampling uncertainty, which is defined as the uncertainty associated with the number and locations of samples collected. As an alternative to traditional investigation tools and approaches, High Resolution Site Characterization (HRSC) applies innovative approaches and characterization tools to better-define contaminant sources and plumes, and develop detailed two- or three-dimensional CSMs to support effective decision making.

Collaborative datasets (i.e., the concept of combining multiple lines of evidence developed using different investigation methods) were developed at two sites in Australia with more than a decade of investigation and/or remediation history. The use of a Lines of Evidence approach and HRSC allowed for addressing data gaps inherent in the previous CSMs and resulted in reductions in business risk, stakeholder concerns, and life-cycle costs.

METHODS

A primary means of reducing sampling uncertainty is through the use of tools that allow for cost-effective collection of more data points than conventional methods allow (eg, Membrane Interface Probe, Laser-Induced Fluorescence, and Hydraulic Profiling Tool). The data collected using these methods can be combined into a collaborative dataset with existing site data collected using traditional investigation tools (eg, soil core descriptions, laboratory analytical data, historical gauging/monitoring data) to build a higher-resolution CSM. The following tools can be used

Laser Induced Fluorescence

The Ultra-Violet Optical Screening Tool (UVOST®) Laser Induced Fluorescence (LIF) is a direct push, real-time, semi-quantitative and qualitative direct sensing tool that uses ultra-violet laser light to cause fluorescence in Light Non-Aqueous Phase Liquids (LNAPLs), which can then be measured. The tool is affixed at the head of a Geoprobe® drill rod string. Laser light is sent through a fiber optic cable placed within the Geoprobe® rods where it exits a sapphire window and strikes the soil matrix as the probe is steadily pushed into the ground. The fluorescence emitted by soil is collected by a second sensor and transmitted via fiber optic cable back up the bore hole to the instrument for detection and analysis. This allows for a continuous profile of fluorescence versus depth to be developed.

Geoprobe® Hydraulic Profiling Tool

The Geoprobe® Hydraulic Profiling Tool (HPT) is a direct-push, real time, semi-quantitative tool that is used to evaluate hydraulic properties of unconsolidated soils. The HPT probe is equipped with a small stainless steel screen that is used to inject water at a constant low flow rate into the formation as the probe is advanced into the subsurface. Injection pressure, which is monitored and plotted with depth, is an indication of the relative hydraulic properties of the soil. The HPT probe is also equipped with an EC probe to measure electrical conductance of the soil and fluids in the soil.

RESULTS

Case Study 1: Residual LNAPL Volume Estimation

Since 1997, several traditional investigations have been completed at a former service station situated in the Adelaide Coastal Plain on Quaternary-aged deposits characterised by heavily fissured clay with sandy clay lenses. Following primary source removal in 2004, an initial decrease in reported dissolved-phase hydrocarbon (DPH) concentrations was observed. However, residual DPH concentrations remained in on- and off-site wells and Light Non-Aqueous Phase Liquid (LNAPL) was measured at apparent thicknesses of more than a meter.

The original CSM was developed using a traditional dataset and contained a number of data gaps relating to the hydrogeological setting of the site and LNAPL architecture and recoverability.

These data gaps were addressed in 2009-10 using a collaborative dataset based on desk top review and traditional monitoring activities coupled with innovative investigation methods such as a passive soil gas survey, Ultra-Violet Optical Screening Tool (UVOST®) Laser-Induced Fluorescence (LIF) and Geoprobe® Hydraulic Profiling Tool (HPT). In particular, Geoprobe® HPT enabled identification of two distinct water-bearing units present beneath the site, a localised perched zone and a deeper zone of greater lateral extent, whilst LIF enabled estimation of residual LNAPL volume within these units.

The updated CSM, developed using the collaborative dataset interpretation, indicated that LNAPL is not present as a continuous layer, but more likely it has been accumulated in naturally occurring fractures and fissures within the tight clay layers, mainly located above the upper perched zone in an area proximal to the former underground storage tank pit.

Case Study 2: LNAPL Recoverability Evaluation

HRSC was conducted at a former service station in Victoria to support a Site Audit Statement to allow for site divestment. The site ceased operation as a service station in 1999, with fuelling infrastructure and adjacent impacted soil removed between 2000 and 2007. Multiple rounds of site characterisation were completed over this period, with remaining uncertainties in the CSM with respect to lateral extent of remaining hydrocarbon, its potential for migration and receptors.

To evaluate risks and LNAPL remedial options, a collaborative dataset was developed using innovative tools such as LIF and Geoprobe® HPT combined with more traditional baildown tests, LNAPL forensics and recoverability assessment, desktop review of a comprehensive data set and a limited number of confirmatory soil borings. Multiple lines of evidence suggested that the DPH was stable, residual impacts were limited to the former UST pit and LNAPL removal has occurred to the extent practicable.

The updated CSM developed by integrating the collaborative dataset with previous assessment results was adequately robust to make decisions regarding the potential for unacceptable risk to receptors and the need for remedial or management actions for the site.

CONCLUSIONS

In each of the case studies described, an improved CSM was developed using a collaborative data set and HRSC tools and approaches. The improved CSMs were used to make decisions based on the potential for plume mobility in the absence of a continuing primary source, potential recoverability of the remaining hydrocarbon, and source-pathway-receptor linkages. This better understanding of the site risk profile allowed for development of a site management plan and/or more focused remediation goals.

DEVELOPMENT OF A THREE DIMENSIONAL HANGING DROP CELL EXPOSURE SYSTEM (HDCES) FOR TOXICOLOGICAL STUDIES

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INTRODUCTION

2D cell model which lacks extensive cell-cell and cell-matrix interactions cannot simulate the physiological response to gaseous chemicals. Three dimensional (3D) model in cell culture, because of its more realistic simulation in tissue functions, has attracted more studies in recent years. Different techniques and methods for making 3D cell model have been developed and commercialised among which the hanging drop (HD) technique (Kelm et al., 2003; Timmins et al., 2004) is straightforward and cost-effective. However, the HD technique has not been widely employed, especially in the area of inhalation research due to several drawbacks. This project aimed to develop a three dimensional (3D) cell bioanalytical system for toxicological studies of air pollutants based on the conventional (HD) technique. A novel exposure apparatus was designed and developed with which the exposure time of the cell can last for over 48 hours. Using the system, we evaluated the activation of Aryl hydrocarbon receptor (AhR) activation using cells harbouring the AhR element. The preliminary results indicated the 3D cells in HD with certain endpoints are a useful model for inhalation toxicology and the novel exposure apparatus will make 3D-hanging drop applicable widely in environmental, toxicological and pharmaceutical studies.

METHODS

Apparatus design: HD cell exposure system (HDCES) was designed based on the conventional HD technique. Conceptual model was designed to satisfy the requirements for gaseous chemical exposure. To achieve the maximum stability of the HD, a cone-shape holder was adopted with its shape optimized by analysis of the relative parameters including gravity force, volume of the droplet, surface tension and viscous force using software (MATLAB). The HD holder attached to a plate was compatible to 96-well plate format. The exposure chamber was designed according to the size of above plate with HD holder. A water reservoir was put in the chamber to keep the moisture. The cells were loaded on the top of plate through the hole of the HD holder. Culture medium was supplemented to the cells through the microchannels using microfluidic technique to maintain the droplets.

Making recombinant cell lines harbouring Aryl hydrocarbon receptor (AhR) element: A549 cells and C3A cells were transfected with reporter plasmid, pGreen1.1 (a kind gift from Professor Michael S Denison, University of California, USA). The plasmid contains the 480-bp dioxin-responsive domain from the mouse CYP1A1 gene inserted upstream of the mouse mammary tumor virus (MMTV) promoter and it confers dioxin responsiveness upon the MMTV promoter and adjacent EGFP reporter gene (Nagy et al., 2002). After transfection, the cells were selected with G418 followed by the screening with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) to get the cell lines (pGreen1.1/C3A and pGreen1.1/A549) with strongest inducibility. The derived stable cell lines were maintained in the medium containing G418. The AhR response activity in these cells was then tested with TCDD and benzo[a]pyrene (B(a)P), benzene and benzene metabolites, hydroquinone and benzoquinone. The cells were cultured to form 3D spheroid in HDCES followed by exposure to gaseous benzene.

RESULTS AND DISCUSSION

(a) HD cell exposure system (HDCES): the design of the HDCES is shown in Fig.1.

In comparison with the conventional HD, HDCES has following unique characteristics: 1) the volume of the medium in the drop can have a range from 30 μL to 300 μL ; 2) more cells can be seeded ($2.5\text{-}7.5 \times 10^3/\text{drop}$) and grow longer time over 48 h; 3) the resuspended droplet is much more stable; 4) the size of the 3D spheroid can be up to 2 mm in diameter which is available for histological study; 5) by supplement with the medium through microchannels, the HD will not be dried by evaporation; and 6) by adjusting the diameter of the HD holder, the 3D cell in the droplet can be easily transferred into 24, 48 and 96 well plate for high-throughput assay.

(b) Benzene induced AhR activation.

(i) Benzene activated AhR in 2D cells (liquid exposure): benzene induced AhR activation is tested by measuring the fluorescent intensity of the cells using a plate reader. Result showed the activation of AhR by benzene at 10 nM.

(ii) Benzene activated AhR in 3D cells (air exposure): AhR activation was found to be induced by gaseous benzene at 10 ppm over 10 hours in HDCES (Fig. 2).

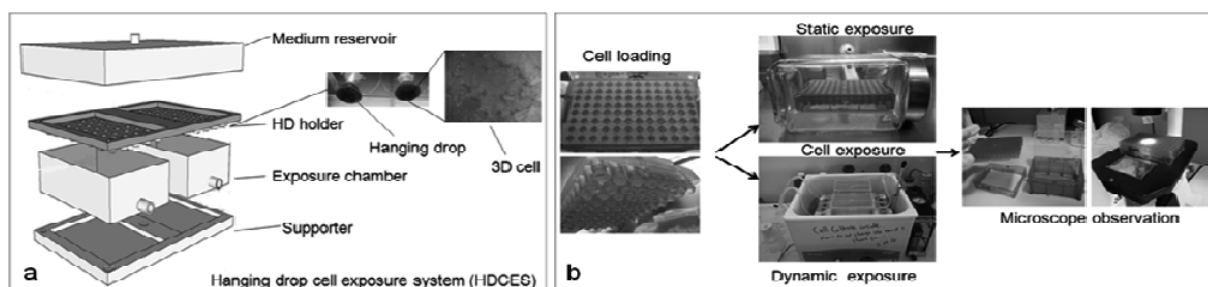


Fig. 1. Hanging drop cell exposure system (HDCES). a. Schematic design of HDCES. b. Prototype of HDCES.

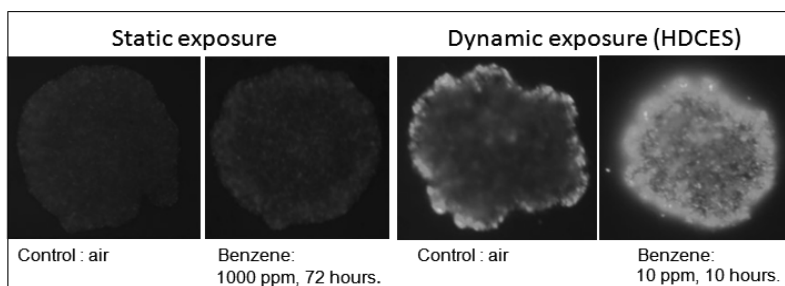


Fig. 2. AhR activation induced by exposure to benzene at 10 ppm in HDCES

CONCLUSIONS

Benzene can induce AhR activation *in vitro* cell culture at relatively low concentration. 3D cell culture in hanging drop with certain endpoints is a novel and useful model for inhalation toxicology. The novel exposure apparatus (HDCES) will make HD technique applicable widely in environmental, toxicological and pharmaceutical studies.

ACKNOWLEDGEMENT

This project is funded by CRC CARE.

REFERENCES

- Kelm, J.M., Timmins, N.E., Brown, C.J., Fussenegger, M., Nielsen, L.K. (2003) Method for generation of in homogeneous multicellular tumor spheroids applicable to a wide variety of cell types. *Biotechnol Bioeng.* 83(2):173-180.
- Nagy, S.R., Sanborn, J.R., Hammock, B.D., Denison, M.S. (2002) Development of a green fluorescent protein-based cell bioassay for the rapid and inexpensive detection and characterization of ah receptor agonists. *Toxicol Sci.* 65(2): 200-210.
- Timmins, N.E., Dietmair, S., Nielsen, L.K. (2004) Hanging-drop multicellular spheroids as a model of tumour angiogenesis. *Angiogenesis.* 7(2):97-103.

HANGING DROP, A NOVO *IN VITRO* AIR BENZENE EXPOSURE MODEL

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INTRODUCTION

A challenge for *in vitro* biological monitoring for barely-water soluble volatile organic compounds is the media barrier effect that shelters the cells from toxic exposure (Ritter et al., 2001). The effects of chronic exposure to benzene on A549 cells have not been adequately monitored because benzene could evaporate from the media in 1 h (Giuliano et al., 2009). Although the CULTEX® *in vitro* cell exposure system mimics *in vivo* respiratory exposure which allows direct contact of the cultured cells with volatile test compounds at a controlled flow rate over a period of time (Aufderheide et al., 2002), this system would only allow exposure time <2 h and is not suitable for longer term exposure-effect studies.

We adopted the hanging drop spheroid culturing method into an air exposure model that achieved an air-liquid inter-phase exposure for over 24 h. Repeatable dose response in both 2D and 3D spheroid cultures was found. Sealed liquid exposure of A549 cells to benzene was also performed and sensitive dose response has been achieved for over 36 h. Interleukin studies of A549 cells exposed to benzene for 24 h have been monitored as well. Preliminary comparison of benzene exposure effect on A549 cells was carried out using the Cultex exposure chamber for 1 h to 2D culture and 3D spheroid culture of A549 cells.

METHODS

Exposure

- Hanging drop exposure was achieved by inoculating lung A549 cells in hanging drops of 20µL size on the inner septum of 40mL volatile organic analysis (VOA) vials (LECO #21796). Benzene was then injected using a 10µL Hamilton syringe to mimic an air benzene exposure chamber.
- Liquid exposure was achieved in 2mL VOA vials (LECO #24620) filled with media using DMSO as carrier vehicle for benzene.
- Benzene air supply to the Cultex exposure system was achieved by feeding 2mL/min laboratory air through a 5mL glass vial with 3 mL initial benzene inside to create an exposure air source in continuous flow.

Assays

- In situ MTS assay** - Cell viability was assayed using the Promega CellTiter 96 Aqueous Non-Radioactive Cell Proliferation (MTS) assay kit (Promega, Alexandria, NSW, Australia) with modifications for *in situ* MTS reaction on the inverted hanging drop before the reaction mix is transferred into a 96 well plate for FLUOstar OPTIMA (Thermo Scientific) absorbance reading at 490nm.
- Comet assay** - Comet Assay kit (Trevigen, Cat# 4250-050-K, Gaithersburg, MD, USA) was used to detect DNA damage of the A549 cells with slight modifications. 3D spheroid cultures were re-suspended before agarose embedding.
- Interleukin** Human interleukin cytokine kit (BD systems #551811) was used to detect IL8, IL-1beta, IL6, IL10, TNF and IL-12p70 and cytokine expression by BD FACSCanto.

RESULTS AND DISCUSSION

- The 2D and 3D air hanging drop air exposure method, as well as sealed liquid benzene exposure, produced repeatable dose response over 6-24 h (Figure 1).

- Total cell death occurred for both control and exposed groups for 2D culture while 3D spheroid culture survived with evidence of DNA damage through comet assay to the exposed group compared to the control (Figure 2).
- Whilst elevation of IL6 and IL8 were observed, no significant difference was found in interleukin expression between the control and benzene exposed groups (data not shown).

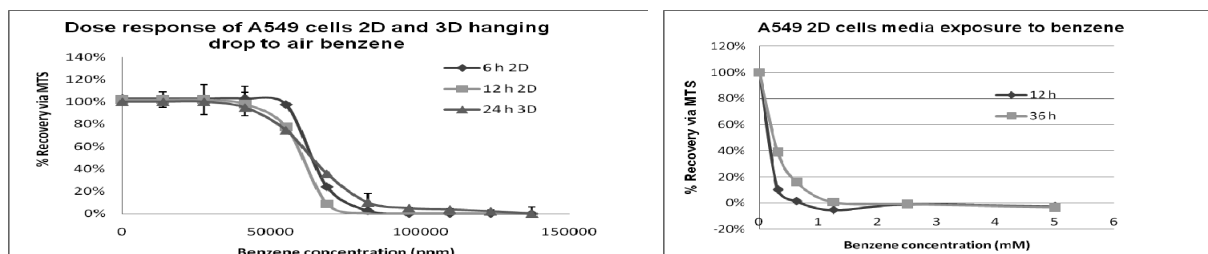


Figure 1. Dose response of A549 cells exposed to benzene in air (left) and in media (right) through hanging drop air exposure and sealed media exposure with DMSO as carrier vehicle.

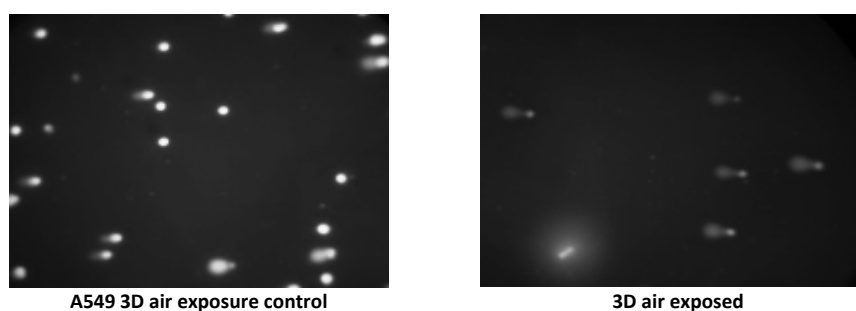


Figure 2. Comet assay of A549 spheroid exposed to benzene through air with evidence of DNA damage (right) compared to the controls (left).

CONCLUSIONS

In conclusion, benzene is toxic and it produces DNA damage to A549 cells. 2D and 3D hanging drop methods have shown preliminary cytotoxicity results of longer time exposure. More research is needed in order to carefully evaluate the hanging drop exposure system, 2D media exposure system in comparison with the commercially available Cultex *in vitro* system to explore the possibility of establishing an *in vitro* chronic air exposure-effect monitoring model. This, in turn will form an essential knowledge background for method development for effective risk-based assessment and management of site contaminants.

ACKNOWLEDGEMENT

This project is funded by CRC CARE.

REFERENCES

- Aufderheide, M., Knebel, J. W., and Ritter, D. (2002) A method for the *in vitro* exposure of human cells to environmental and complex gaseous mixtures. In: Application to various types of atmosphere. *Atla-Alternatives to Laboratory Animals* 30: 433-441.
- Giuliano, M., Stellavato, A., Cammarota, M., Lamberti, M., Miraglia, N., Sannolo, N., and De Rosa, M. (2009) Effects of low concentrations of benzene on human lung cells *in vitro*. *Toxicology Letters* 188:130-136.
- Ritter, D., Knebel, J. W., and Aufderheide, M. (2001) *In vitro* exposure of isolated cells to native gaseous compounds - Development and validation of an optimized system for human lung cells. *Experimental and Toxicologic Pathology* 53: 373-386.

IMPROVED *IN-VITRO* TOXICOLOGY OF INHALABLE IRON-RICH PARTICLES FROM MINING INDUSTRIES

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INTRODUCTION

Increasing activity in Australian mining industries could lead to increasing exposure of populations to airborne dusts. However, the immediate and long term effects of this are only approximately understood and regulated through toxicity studies conducted overseas, on dusts which may not represent the characteristics of Australian mineral dusts (Green, 2002).

This study investigated toxicological effects of PM₁₀ (<10 µm) iron-rich particles from Port Hedland. Improved *in-vitro* techniques were used to better reflect *in-vivo* toxicology, while still being suited field monitoring adaptation (Bakand et al., 2007). Human cell line cultures of lung epithelial cells (A549), lung fibroblast cells (LL24) and macrophages (U937) were tested for combinations of cytotoxicity, cytokine stimulation and morphology, to exposures of iron-rich PM₁₀, as well as standards of iron(III), copper and titanium oxides, <5 µm in size.

METHODS

Cytotoxicity

Cytotoxicity measurements were conducted using cell cultures split onto 96-well plates at 80% confluency and exposed to serial dilutions of particle suspensions in media, using the Promega CellTiter 96® Aqueous One Solution Cell Proliferation Assay (MTS), a colorimetric cell proliferation assay. U937 was differentiated with 3 ng/µL of phorbol myristic acid 48 h before exposures.

Cytokine Production

Cytokine measurements were conducted on media supernatants from exposed cell cultures in 96 well plates as described for cytotoxicity assays. The supernatants were analysed for cytokines IL-8, IL-1beta, IL-6, IL-10, TNF and IL-12p70 using a BD™ Cytometric Bead Array (CBA) Human Inflammatory Cytokines Kit, measured on a BD FACSCanto™ flow cytometer.

Electron Microscopy

Cell cultures were split onto 6 well plates at 80% confluency and exposed to particle suspensions in media. The cells were then fixed and encased in resin caps for ultramicrotomy at 60 nm. Cells were then imaged using a JEOL 1010 Transmission Electron Microscope.

RESULTS AND DISCUSSION

Cytotoxic sensitivity of cells to iron-rich PM₁₀ increased up to twofold with addition of 1% DMSO as a particle dispersant to mimic the effect of lung fluids; macrophages were most sensitive cell type recording an IC₅₀ of ~230 µg/cm² over 24 h, but still concordant with other lung cell responses (data not shown). This toxicity was moderate compared to copper oxide standards (~10 µg/cm²) but higher than iron oxide standards (~340 µg/cm²). Cytokine measurements indicated lung epithelial cells reacted marginally to particles, while macrophages reacted measurably and differentially to particle composition in a relatively short timeframe, illustrated in Fig. 1.

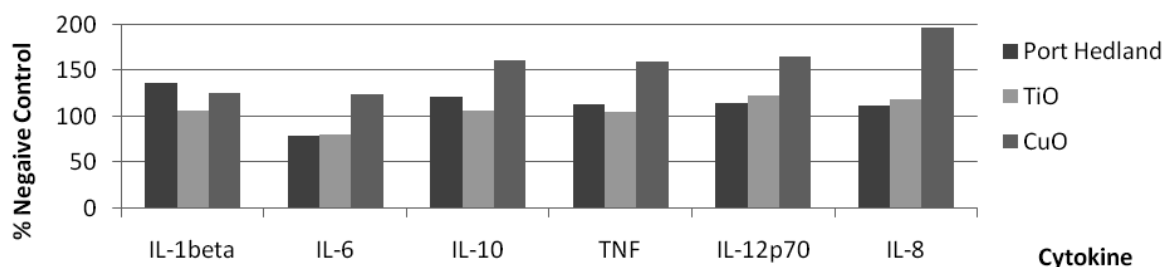


Fig. 1. Cytokine expression corrected for cell death of differentiated U937 cells exposed to TiO and CuO <math>< 5 \mu\text{m}</math> particles and iron-rich PM10 at

Light microscopy showed lung fibroblasts caused agglomeration of particles greater than other cell types and changed morphology. Electron microscopy further showed interaction between cell membranes and particles, including particle uptake. This is outlined in Fig. 2.

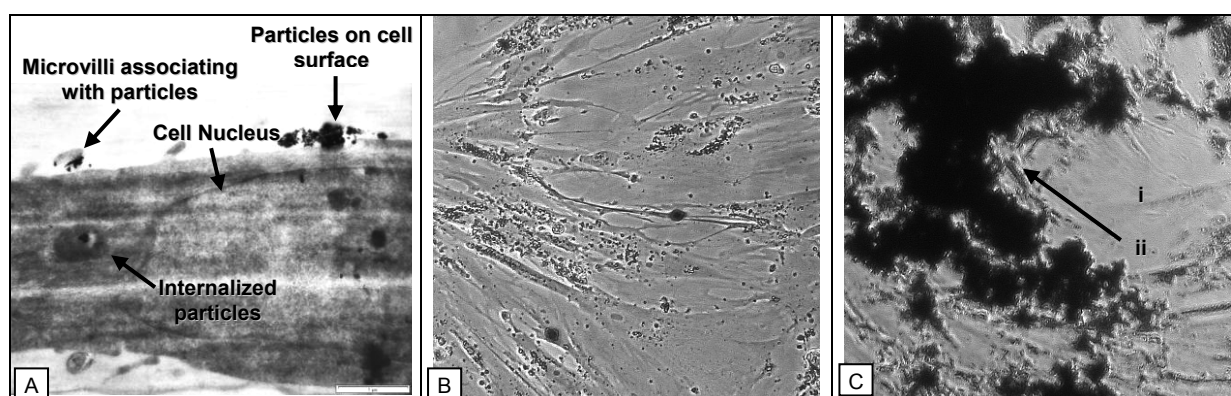


Fig. 2. A) TEM image (

CONCLUSIONS

Depending on exposure duration and concentration, iron-rich PM10 can lead to inflammation and fibrosis in a clinical setting, given the observed cytotoxicities and cytokine expressions across lung cell types (Sayes et al. 2007). Morphological changes in fibroblasts and inclusion bodies found in epithelial cells responding to particle exposure further support this outcome. Continued study of different parameters and improvements to *in vitro* techniques replicating lung tissues and fluids will improve sensitivity (contributed to by the size heterogeneity of PM10 samples when dispersed) and will ultimately help devise Australian airborne PM10 limits relevant to iron-ore mining and handling industries.

REFERENCES

- Green, L., (2002). What's Wrong with the National Ambient Air Quality Standard (NAAQS) for Fine Particulate Matter (PM_{2.5})? *Regulatory Toxicology and Pharmacology* 35(3): 327-337.
- Bakand, S., Hayes, A. & Winder, C., (2007). An integrated *in vitro* approach for toxicity testing of airborne contaminants. *Journal of toxicology and environmental health Part A* 70(19): 1604-12.
- Sayes, C.M., Reed, K.L. & Warheit, D.B., (2007). Assessing toxicity of fine and nanoparticles: comparing *in vitro* measurements to *in vivo* pulmonary toxicity profiles. *Toxicological sciences* 97(1): 163-80.

This project is funded by CRC-CARE

TOXICITY OF USED AND FRESH ENGINE OILS TO EARTHWORM SURVIVAL AND SOIL HEALTH

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INTRODUCTION

Leakage of engine oil from the automobile engines in the parking areas, roadways or other places, accidental spillages, and improper handling or disposal leads to contamination of soil and water thereby posing risk to the ecosystem health. The waste engine oils are classified as one of the most hazardous mainstream categories of environmental pollutants. Chemical analyses in conjunction with toxicological assays provide better understanding of the toxic effects of the contaminants, their bioavailability and associated risk (Megharaj et al., 2000). But only few studies are available on the integrated toxicity studies about used engine oil impact on soil biota and soil health. Hence, the present study was conducted to evaluate the effect of used engine oil to earthworm and soil health in comparison with fresh engine oil.

METHODS

The toxicity of used and unused engine oils to soil health was determined following an integrated approach using the standard OECD protocols. Thus, the toxicity parameters used in the toxicity testing included earthworm mortality, hydrocarbon bioaccumulation, soil enzyme activities (dehydrogenase and potential nitrification) and hydrocarbon quantification. Hydrocarbon concentrations in soil and worm tissues were solvent extracted and quantified using GC-FID and GC-MS.

RESULTS AND DISCUSSION

The composition of used and unused engine oils varied significantly as determined by GC-MS. The variation can be seen clearly by the differences in the chromatographic peaks, humps and concentrations (Fig.1& 2). Some short chain carbon compound peaks found in the used engine oil were absent in the fresh oil. The variation between the two oils is furthermore explained through the dissimilarity in their water accommodated extracts and alkali extracts. The Used engine oil extract contains more BTEX and PAH compounds which are not detected in the fresh engine oil (Fig.2).

The median lethal concentration (LC₅₀) of used engine oil and fresh engine oil for earthworm differed greatly. Thus the LC₅₀ values for used and fresh engine oils were 0.52 ± 0.02 and 4.8 ± 0.1 %, respectively. The fresh engine oil enhanced the earthworm body weight even at the higher doses but not so in the case of used engine oil. The toxicity of the used engine oil can be ascribed to the presence of a mixture of more complex toxic compounds like aliphatic and aromatic hydrocarbons including volatile aromatics and PAHs, heavy metals, PCBs and other compounds. Addition of engine oils to the soil resulted in significant changes in soil enzyme activities even within the short exposure time. Both the fresh and used engine oil addition influenced the activities of the hydrolytic enzymes and potential nitrification (ammonium oxidation) rate in the soil; the change became significant even at low concentration of the used engine oil. The measured soil quality parameters such as soil DHA and urease activities showed significant enhancement at lower oil concentrations and inhibition at higher oil concentrations. The used engine oil is toxic to potential nitrification rate at 0.05 % whereas the fresh unused oil becomes toxic only at 1.5 %. This clearly shows that the used engine oil is more toxic to the nitrifiers than the fresh engine oil. The toxic compounds in the used oil might be the hydrocarbons mainly the volatile aromatics and the

PAHs, heavy metals, PCBs or any other compounds. Oil hydrocarbons affect the nitrification activity by reacting with the ammonia monooxygenase (AMO) enzyme. Hydrocarbons cause inhibition through competitive or non competitive interactions with this enzyme (Keener and Arp, 1993). This study also showed that earthworm inoculation to the engine oil polluted soils had positive influence on the soil enzyme activity and nitrification rate.

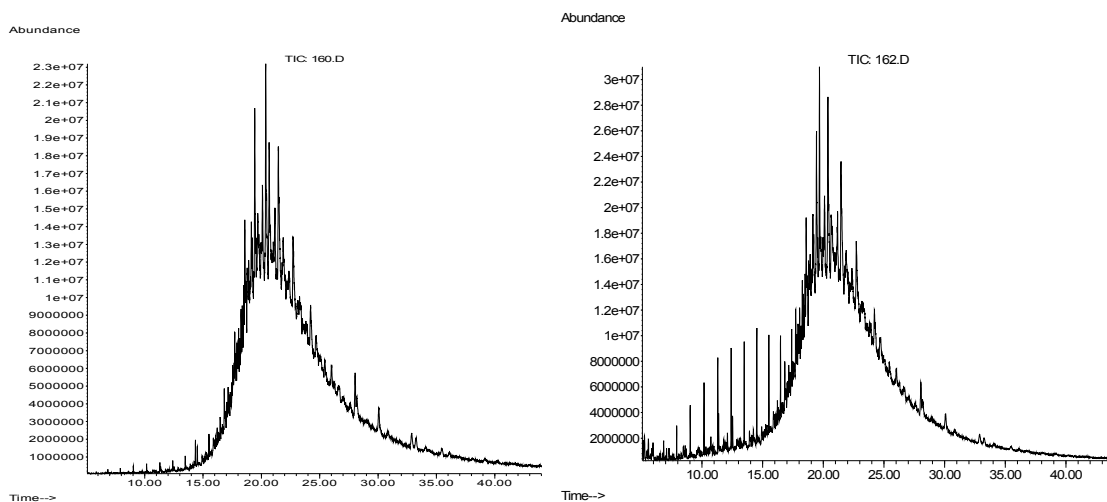


Fig. 1 The variation between the fresh and used engine oils as shown by the GC-MS chromatogram

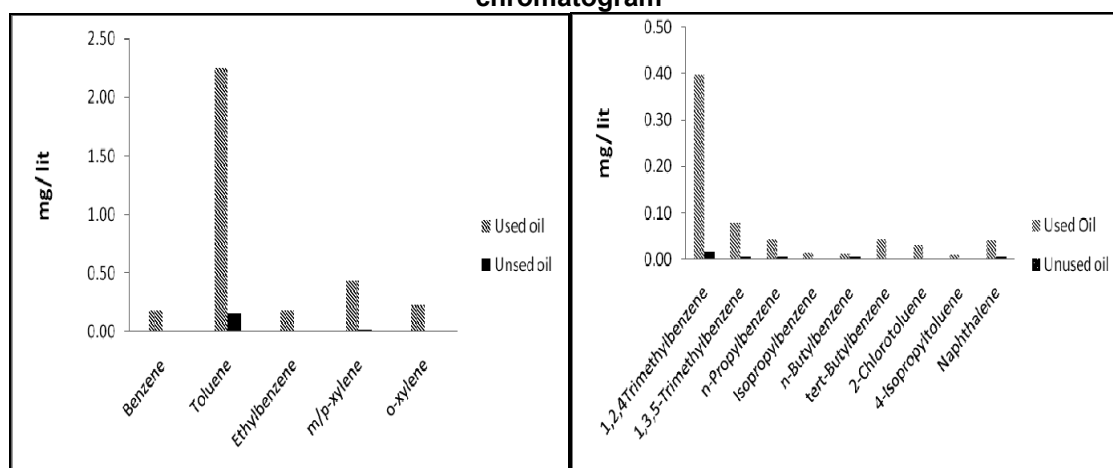


Fig. 2 BTEX and other volatile aromatics in water extracts of used and unused engine oils

CONCLUSIONS

This study clearly demonstrated that the used engine oil is more toxic than fresh engine oil to earthworm and soil enzyme activities. Since the petroleum hydrocarbons and other toxic compounds from the used engine oil are a major threat to soil biota and soil health, used engine oil is considering as soil quality decliner, when enters into the soil.

REFERENCES

- Keener WK, Arp DJ. 1993. Kinetic studies of ammonia monooxygenase inhibition in *Nitrosomonas-Europaea* by hydrocarbons and halogenated hydrocarbons in an optimized whole-cell assay. *Appl Environ Microbiol* 59:2501–2510.
- Megharaj M, Singleton I, McClure NC, Naidu R. 2000. Influence of petroleum hydrocarbon contamination on microalgae and microbial activities in a long-term contaminated soil. *Arch Environ Contam Toxicol* 38: 439-445.
- Organization for Economic Co-operation and Development. 1984. Earthworm, acute toxicity tests. OECD Guideline for Testing of Chemicals 207. Paris, France.

TOXICITY OF POLYAROMATIC HYDROCARBONS AND HEAVY METALS ALONE AND IN COMBINATION TO MICROALGA

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INTRODUCTION

Polyaromatic hydrocarbons (PAHs) are a group of toxic persistent pollutants. They are released into the environment both naturally and as a result of anthropogenic activities. Similarly heavy metals are also released into the environment via both natural and anthropogenic sources. Generally, PAHs co-exist with heavy metals in most of the PAH contaminated sites and in particular manufactured gas plant (MGP) sites (Thavamani et al., 2011). The presence of PAH and heavy metal mixtures have been reported in aquatic (Brown and Peake, 2006) and soil environments (Mielke et al., 2001). PAHs and heavy metals present together can increase the toxicity as both are highly toxic with different modes of action in producing toxic effects to the organisms. In order to understand the real toxicity of mix contaminated sites, toxicity studies should be carried out for pollutant mixtures. In contrast, most toxicity studies have been carried out only for individual chemicals. In view of this we attempted to evaluate the toxicity of a pollutant mixture, comprising of phenanthrene, benzo[a]pyrene, cadmium and lead. Microalga, *Chlorococcum* sp. was used as the model organism to study the toxicity. The interaction between the pollutants in exerting the toxicity was assessed using the full 2ⁿ factorial design.

METHODS

The microalga *Chlorococcum* sp. isolated from South Australian soil was used in this study. For the statistical analysis, higher and lower limits of the PAHs and heavy metals were fixed at 5000 ppb and 50 ppb. A 2ⁿ full factorial design experiment was carried out with 16 experiments and two replicates. Microalga was exposed to the Bold's basal medium spiked with pollutants alone and in various combinations for 96 hrs. Cells were counted in the haemocytometer at the end of incubation. All the statistical analysis was carried out using Minitab 16 software.

RESULTS AND DISCUSSION

At the chosen concentration 50-5000 µg/L, lead is more toxic to *Chlorococcum* sp. followed by BaP and cadmium. Among the four chemicals chosen in this study phenanthrene was found to be less toxic. It is clearly evident from the normal plot of the standardized effects that there is a significant interaction between the PAHs and heavy metals in exerting the toxicity (Fig.1). The present study elaborates the potential of factorial design approach in assessing the toxicity using the microalga. This study shows that the effect of individual chemicals on exerting toxicity is higher when compared to the interaction effects. It is apparent from the Table.1 that the three-way interactions between the chemicals has negative impact on the growth of *Chlorococcum* sp. in contrast to the four-way and two-way interactions that exhibited positive impact. This clearly demonstrates that the mixture toxicity to microalga (synergistic or antagonistic) varies from positive to negative depending on the nature of pollutant combinations.

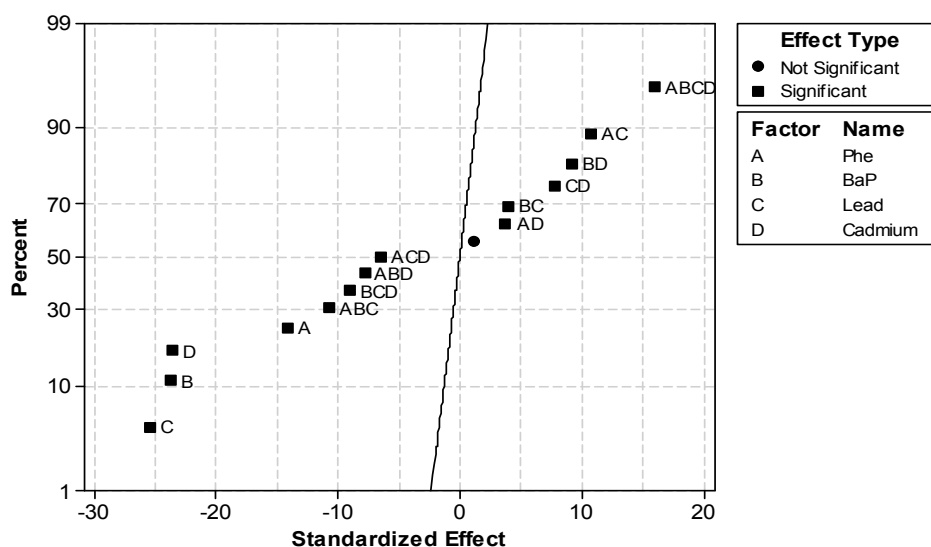


Fig. 1. Normal effects plot showing the statistical significance of main and interaction effects of PAHs and heavy metals on growth of *Chlorococcum* sp.

Table.1. Estimated effects and coefficients for the growth of *Chlorococcum* sp. in the presence of PAHs and metal mixture

Factors and Interactions	Net effect	p-Value
Phenanthrene (Phe)	-52.44	0.000
Benzo[a]pyrene (BaP)	-88.56	0.000
Cadmium (Cd)	-94.81	0.000
Lead (Pb)	-88.06	0.000
Phe*BaP	4.31	0.264
Phe*Pb	40.06	0.000
Phe*Cd	14.06	0.002
BaP*Pb	14.69	0.001
BaP*Cd	34.19	0.000
Pb*Cd	28.94	0.000
Phe*BaP*Pb	-39.94	0.000
Phe*BaP*Cd	-29.19	0.000
Phe*Pb*Cd	-23.94	0.000
BaP*Pb*Cd	-33.56	0.000
Phe*BaP*Pb*Cd	59.56	0.000

CONCLUSIONS

Factorial design experiment can be used to assess the toxicity of mixed pollutants to microalgae. The combined toxicity of PAHs and metals to microalga varies depending on the nature of the chemicals and their combinations.

REFERENCES

- Mielke, H.W., Wang, G., Gonzales, C.R., Le B, Quach V.N., Mielke P.W. (2001) PAH and metal mixtures in New Orleans soils and sediments. *Sci Total Environ.* 281: 217-227.
- Brown, J.N., Peake, B.M., (2006) Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Sci Total Environ.* 359:145-155.
- Thavamani, P., Megharaj, M., McFarland, R., Naidu, R. (2011) Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: implications to bioremediation. *Environ Int* 37: 184-189.

EFFECTS OF CONTAMINANTS ON HUMAN HEALTH AND PERSISTENT ORGANIC POLLUTANTS IN HONG KONG MOTHERS

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INTRODUCTION

Persistent organic pollutants (POPs) are lipophilic compounds with a long half-life. They are widely distributed in the environment and are harmful to the ecosystem. Some are confirmed or suspected human carcinogens, while others may exert direct or indirect toxic effects to our health. They can enter the food chain and accumulate in our body. Monitoring of POPs in human milk has been used to assess our exposure to these chemicals.

METHODS

From February to August 2009, we collected 146 samples of milk from Hong Kong mothers who had given birth to their first babies (primiparae). Milk samples were analyzed individually for 'analytically simple' POPs: aldrin, chlordane, dieldrin, dichlorodiphenyltrichloroethane (DDT), endrin, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachlorocyclohexane (HCH), toxaphene congeners, polychlorinated biphenyls (PCBs), and mirex. Samples were pooled (by the mothers' age and duration of stay in Hong Kong) into four 'pools' (1=HK mothers aged <30 years, 2=HK mothers aged ≥ 30 ; 3=Chinese migrants aged <30, 4=Mainland China migrants aged ≥ 30) for the determination of these POPs, dioxins (PCDDs), furans (PCDFs) and dioxin-like PCBs. High-resolution gas chromatography (HRGC) / high-resolution mass spectroscopy (HRMS) was performed. Concentrations of dioxins, furans and PCBs were calculated for individual pollutants and collectively, using their respective toxic equivalent factors (TEF) determined by the WHO in 1998, to calculate the overall toxic equivalence (TEQ) as WHO-PCDD/F-TEQ and WHO-PCB-TEQ. Mothers were surveyed for their dietary histories and other personal, occupational and household information. Associations were sought between the mothers' levels of 'simple' POPs and their dietary intake of meat, fish and other seafood, eggs and dairy products.

RESULTS AND DISCUSSION

Among POPs detected in breast milk are most members of the DDT group (except o,p'-DDD and o,p'-DDE), oxy-chlordane (except alpha- and gamma-chlordane), trans-nonachlor, dieldrin, the HCH group (except gamma-HCH), two toxaphene congeners (Parlar 26 and 50) and mirex. Aldrin, Parlar 62, the endrin group and heptachlor group were not detected in all samples.

Of all POPs tested, total DDT had the highest concentrations (per gram lipid weight) in all pooled samples, at 759.9 ng/g, 1132.3 ng/g, 956.4 ng/g and 1321.0 ng/g in pools 1 to 4 respectively, and a weighted mean of 998.8 ng/g. p,p'-DDE constituted 84-85% of total DDT.

Beta-HCH was the second highest, at 232.4 ng/g, 477.5 ng/g, 156.1 ng/g and 346.5 ng/g in pools 1–4 were respectively, and a weighted mean of 302.2 ng/g. Levels of most POPs were higher in older mothers (pools 2 and 4) than younger mothers (pools 1 and 3). Hong Kong mothers had lower levels of DDT (total DDT, p,p'-DDE and p,p'-DDT) than mainland China migrants, suggesting that food contamination by DDT was more serious in mainland China. Similar findings were observed for hexachlorobenzene (HCB). For 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the concentrations in pools 1–4 were: 0.91 pg/g, 0.98 pg/g, 0.87 pg/g and 0.98 pg/g respectively, with a weighted mean of 0.934 pg/g. In pools 1–4, the levels of dioxins and furans expressed as WHO-PCDD/F-TEQ were: 6.56 pg/g, 8.32 pg/g, 7.90 pg/g and 7.68 pg/g, with a weighted mean of 7.48 pg/g. The levels of dioxin-like PCBs expressed as WHO-PCB-TEQ from pool 1–4 were: 3.28 pg/g, 5.07 pg/g, 2.93 pg/g and 3.92 pg/g, with a weighted mean of 3.79 pg/g. The levels of dioxins, furans and dioxin-like PCBs expressed as WHO-PCDD/F-PCB-TEQ were 9.84 pg/g, 13.38 pg/g, 10.83 pg/g, and 11.60 pg/g respectively (weighted mean: 11.27 pg/g).

Significant positive associations were observed for the following personal risk factors: maternal age with levels of alpha-HCH, beta-HCH, dieldrin, toxaphene congener Parlar 50, *trans*-nonachlor, PCB 153 and PCB 138; the frequency of intake of fish with levels of p,p'-DDT and toxaphene congener Parlar 50; the frequency of poultry intake with dieldrin, toxaphene congener Parlar 50 and all three PCBs (28, 153 and 138); having eaten sea mammals with beta-HCH; and the frequency of intake of other seafood (than fish) with *trans*-nonachlor. Statistically significant but negative associations were also observed for food frequencies of some food with several POPs. Human uptake of dioxins and other POPs is mostly from contaminated food. Low concentrations of dioxins are also present in the air but inhalation is a minor route of dioxin intake.

Compared to previous local studies, the concentrations of DDT (and its metabolites) and beta-HCH this study have declined steadily over the past decades, by about 40% for DDT and about 68% for beta-HCH compared to our 2002 study of Hong Kong and migrant mothers (Hui et al, 2008; Hedley et al., 2010). Likewise, the mean concentrations were 9% lower for PCDD/F, 20% lower for PCB, and 13% lower for total TEQ compared to levels reported in our 2002 study (Hedley et al, 2006).

CONCLUSIONS

The presence of many POPs in human milk implies their ubiquitous distribution in the environment. A better understanding of human exposure to POPs will help in the development of policies and strategies for the elimination or reduction of emissions of POPs into the environment. In addition, surveillance of POPs in common foodstuff, combined with regular dietary surveys of different population groups, will provide the basis for health risk assessment of the Hong Kong population.

REFERENCES

- Hui LL, Hedley AJ, Kypke K, Cowling BJ, Nelson EAS, Wong TW, van Leeuwen FXR. DDT levels in human milk in Hong Kong, 2001–02. *Chemosphere* 2008; 73:50–55.
- Hedley AJ, Hui LL, Kypke K, Malisch R, van Leeuwen FXR, Moyd G,1, Wong TW, Nelson EAS. Residues of persistent organic pollutants (POPs) in human milk in Hong Kong. *Chemosphere* 2010; 79:259–265.
- Hedley AJ, Wong TW, Hui LL, Malisch R, Nelson EAS. Breast milk dioxins in Hong Kong and Pearl River Delta. *Environmental Health Perspectives* 2006; 114 (2):202-08.

IMPACT OF ENVIRONMENTAL POLLUTION ON HUMAN HEALTH — SHOULD HEALTH CARE DELIVERY SYSTEM BE RADICALLY REFORMED?

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INTRODUCTION

An increasing incidence of unexplained intractable illnesses in children and infants in Hong Kong has prompted this research. Mercury overload from consumption of fish has been identified as the major culprit. Over a period of nine years in my private paediatric practice, these intractable illnesses have been managed by an innovative therapy with nutritional supplementation and detoxification. The result has been rewarding and cost effective. The lack of awareness of this link in orthodox medicine might be responsible for the escalating incidence of chronic diseases worldwide (World Health Organization, 2010; Stevens & Siegel, 2007).

METHODS

Notable examples of a spectrum of intractable illnesses in infants and children are stunted growth, hyperirritability, tics, attention deficit, hyperactivity, autism, severe allergies, sleep disturbances, mood disorders and autoimmune diseases. Diseases of obscure origin like Kawasaki Disease and recurrent infection can be explained by the concept of toxic overload. Pollutant overload was indicated when there was a dietary history of excessive consumption of seafood or Chinese herbs. Diagnosis was confirmed by performing the urine porphyrins test, hair mineral analysis, or the provoked urine challenge test. The treatment regime included avoidance of the source of toxic input, use of nutritional supplementation or chelation therapy.

The micronutrients zinc, magnesium and selenium are frequently deficient in these patients and supplementation is usually given. Probiotics, omega 3 fatty acids, anti-oxidant and vitamin B complex are frequently given as adjunct therapy to facilitate cure.

RESULTS AND DISCUSSION

The treated patients responded favorably with remission of the intractable illness and often showed catch up growth and improved neurocognitive function. In Hong Kong, more infants have exhibited stunted growth and delayed neurodevelopment with no apparent cause in recent years. The mothers have eaten more fish and bird's nest during pregnancy intending to upgrade the baby's health. This popular practice inadvertently delivered a substantial toxic load of pollutants to the fetus (Bjornberg, 2003). The fetal origin of chronic diseases has been recognized in recent years from decades of observational research (Harding, 2001). The injury to the fetus due to the onslaught of pollutant has barely been appreciated by the public and the healthcare profession. To minimize the impact of environmental toxicant on human health, the best time for intervention is the fetal period. To prevent chronic diseases, an effective measure might be protecting the fetus in utero against any toxic effect of environmental pollutants. Ideally the prospective mothers should undergo screening for toxic overload while contemplating pregnancy and detoxification should be carried out for those affected. Discretion on diet and life style modification should be observed during pregnancy to minimize toxic input to the fetus. Healthy infants with advanced neurocognitive functions have been delivered with this procedure. This phenomenon has demonstrated the principles of the science of "Epigenetics" (Waterland, 2009).

The genome dynamically responds to the environment. By manipulating adverse environmental factors, genetic diseases can be alleviated or even prevented. This novel management of paediatric illnesses has been extended to treat adults with chronic illnesses. The result has excelled that of conventional medical practice. Notable examples were the reversal of essential hypertension or adult onset diabetes after this novel therapy. Autoimmune diseases can be radically cured. There was no need for life long medication. Due to vested financial interest in patent pharmaceuticals, the medical profession does not acknowledge the use of nutritional supplements and control of environment for health restoration.

CONCLUSION

Emerging environmental pollution has adversely impacted human health. The sustainability of conventional healthcare system is at stake. A radical reform of our healthcare system would be imperative in light of this observational study.

REFERENCES

- Bjornberg KA et al (2003) Methylmercury and inorganic mercury in Swedish pregnant women and in cord blood: influence of fish consumption. *Environ Health Perspect* 111: 637-641.
- Harding JE (2001) The Nutritional Basis of fetal origins of adult diseases. *Intern J Epidemiol* 30: 15-23.
- Stevens D, Siegel K (2007) Global interest in addressing non-communicable diseases. *Lancet* 370 (9603): 1901-1902.
- Waterland RA (2009) Early environmental effects on epigenetic regulation in humans. *Epigenetics* 4: 523-525.
- World Health Organization (2010) Global status on non-communicable diseases.

ARSENICOSIS IN CAMBODIA FROM EXPOSURE TO ARSENIC IN GROUNDWATER

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INTRODUCTION

Natural, inorganic arsenic contamination of groundwater threatens the health of more than 100 million people worldwide, including residents of the densely populated river deltas of Asia and Southeast Asia. Arsenic can be found in geological formations associated with river deposit of young Holocene sediments rich in organic content. Reducing groundwater aquifer condition promotes decomposition of the organic carbon through anaerobic microbial respiration which mobilizes inorganic arsenic from host minerals, notably iron oxides.^{1,2} In Asia, high arsenic concentrations have been found in the aquifers of Bangladesh, West Bengal, Nepal, China, Cambodia and Vietnam.¹ The use of arsenic contaminated groundwater in Bangladesh has led to what has been described as the worst mass poisoning of a human population in history, where over 100,000 Bangladeshis have developed skin lesions.^{2,3}

HEALTH EFFECTS OF ARSENIC EXPOSURE

The inorganic salts of arsenic are tasteless and odourless making its contamination in drinking water unsuspecting to the consumers. Soluble inorganic arsenic is acutely toxic, and ingestion of large doses leads to gastrointestinal symptoms, dysfunction of the cardiovascular and nervous systems, and eventually death. In survivors, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy may be observed. Chronic exposure to arsenic in drinking-water is causally related to skin changes such as hyperkeratosis and pigmentation changes, as well as a severe form of peripheral vascular disease known as blackfoot disease.⁴ Chronic exposure also lead to increased risks of cancers of the skin, lungs, bladder, kidney and liver. There are evidences that chronic exposure may also be related to hypertension, cerebrovascular disease, diabetes, reproductive effects, neurological effects and cancers at other sites.^{5,6,7} Increased risks of lung and bladder cancers and of arsenic-associated skin lesions have been reported to be associated with ingestion of drinking-water at concentrations $\leq 50 \mu\text{g/L}$, which is the present arsenic in drinking water guideline for countries like Bangladesh and Cambodia.⁴ The World Health Organisation guideline level is $10 \mu\text{g/L}$.

ARSENICOSIS IN CAMBODIA

UNU-IIGH is leading a team of researchers from Malaysia, South Korea, Hong Kong and Cambodia in assessing the health risk and health care cost of arsenicosis in Cambodia. The Mekong River has a large catchment area, draining weathered arsenic-bearing rocks in the Himalayan and Tibetan highlands.⁸ Only 34% of rural Cambodians have access to bacteriologically safe drinking water. This led the Cambodian Government and partner agencies to install tube wells which were later found to be arsenic contaminated in 2001.⁹ The first cases of arsenicosis were discovered in August 2006.¹⁰ Some 54% of the tube well water samples from the contaminated provinces of Kandal and Prey Veng has arsenic concentrations above $10 \mu\text{g/L}$, with maximum concentrations as high as 900 and 1543 $\mu\text{g/L}$.^{10,11} Based on these elevated arsenic concentrations, the lifetime excess cancer risk may be as high as 2 cancers per 1000 exposed population.¹⁰ In the most polluted Kandal Province, 100% of the population had cancer risk of greater than 1 in 10,000, compared to the moderately polluted Kratie Province where 33.7% of the population had cancer risk of

greater than 1 in 10,000, while in the least polluted Kampong Cham Province, all of the population had cancer below 1 in 10,000, which is considered as the highest acceptable or tolerable cancer risk for the general population.¹²

CONCLUSION

The health and economic burden of arsenicosis in Cambodia has not been fully realised. This is mainly due to the lack of documentation on the prevalence of arsenicosis which, due to its chronicity, is yet to make their physical presence in the exposed communities. Preliminary results indicate that the clinical arsenicosis prevalence rate was as high as 31.2 % in the most contaminated province in Cambodia, and an overall prevalence rate of 11.9 %. In Cambodia, where infant and under-5 mortality rates are 70 and 91 per 1000 live births, respectively, the problem of arsenicosis will not be an immediate health priority.¹³ Nevertheless, its cancer-causing potential of 2 in a thousand is equally alarming which may exert a significant economic burden on the country in the future.

REFERENCES

1. Winkel, L. *et al.* (2008). Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. *Nature Geoscience*, **1**: 536-542.
2. Charlet, L. and Polya D.A. (2006). Arsenic in shallow, reducing groundwaters in Southern Asia: An environmental health disaster. *Elements*, **2**: 91-96.
3. Smith, A.H., Lingas E.O. and Rahman, M. (2000). Contamination of drinking water by arsenic in Bangladesh: a public health emergency. *Bulletin of the World Health Organization*, **78**: 1093-1103.
4. International Programme on Chemical Safety (IPCS). (2001). *Environmental Health Criteria 224: Arsenic and arsenic compounds*. Geneva: World Health Organisation.
5. National Research Council (2001). *Arsenic in Drinking Water 2001 Update*. Washington DC: National Academy Press.
6. Tchounwou, P.B., Patlolla, A.K. and Centeno, J.A. (2003). Carcinogenic and systemic health effects associated with arsenic exposure – a critical review. *Toxicol. Pathol.*, **31**: 575-588.
7. Brinkel, J., Khan, M.M.H. and Kraemer, A. (2009). A systematic review of arsenic exposure and its social and mental health effects with special reference to Bangladesh. *Int. J. Environ. Res. Public Health*, **6**: 1609-1619.
8. Polya, D.A., Gault, A.G., Diebe, N., Feldman, P., Rosenboom, J.W., Gilligan, E., Fredericks, D., Milton, A.H., Sampson, M., Rowland, H.A.L., Lythgoe, P.R., Jones, J.C., Middleton, C. and Cooke, D.A. (2005). *Mineralogical Magazine*, **69(5)**: 807-823.
9. Feldman, P.R., Rosenboom, J-W., Saray, M., Navuth, P., Samnang, C. and Iddings, S. (2007). Assessment of the chemical quality of drinking water in Cambodia. *Journal of Water and Health*, **5.1**: 101-116.
10. Sthiannopkao, S., Kim, K-W., Cho, K.H., Wantala, K., Sotham, S., Sokuntheara, C. and Kim, J.H. (2010). Arsenic levels in human hair, Kandal Province, Cambodia: The influences of groundwater arsenic, consumption period, age and gender. *Applied Geochemistry*, **25**: 81-90.
11. Sthiannopkao, S., Kim, K.W., Sotham, S. and Choup, S. (2008). Arsenic and manganese in tube well waters of Prey Veng and Kandal Provinces, Cambodia. *Applied Geochemistry*, **23**: 1086-1093.
12. Phan K. Sthiannopkao S., Kim K.W., Wong M.H., Sao V., Jamal H.H., Mohamed Salleh M.Y., Syed Mohamed A. 2010. Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway. *Water Research*, **44(19)**: 5777-5788.
13. World Health Organisation (2009). *World Health Statistics 2009*.

PERSISTENT ORGANIC POLLUTANTS IN THE PEARL RIVER DELTA (SOUTH CHINA): ENVIRONMENTAL PROCESSES AND POTENTIAL HEALTH RISK VIA SEAFOOD CONSUMPTION

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Persistent organic pollutants (POPs) targeted by the Stockholm Convention are known to persist in the environment, bioaccumulate in biota, and pose hazard to the ecological system and human health. To assess the effectiveness of policies to reduce and eliminate the release of POPs into the environment, the Stockholm Convention has promoted a global monitoring program. Conversely, understanding the regional geochemical processes and potential health risk of these toxic chemicals is key to the adoption of effective measures to mitigate the adverse effects of POPs globally. In this regard, the Pearl River Delta (PRD), one of the most agriculturally developed and economically advanced regions of China, provides a perfect stage for regional monitoring of POPs. In the last few years, we have conducted a series of studies on the occurrence of selected POPs in various environmental compartments of the PRD. The results from these studies, combined with previously acquired data, allow an integrated assessment of the regional dynamics of POPs in the PRD and dietary intake (and potential human health risk) for local consumers through consumption of seafood products.

We selected 1,1,1-trichloro-2,2-bis(chlorophenyl)ethane (*p,p'*-DDT) and decabromodiphenyl ether (BDE-209) as the model compounds to reconstruct their mass transport budgets and predict their temporal evolutions in soil inventory. Modeling results indicated that residual *p,p'*-DDT, mostly related to historical use, had largely settled into soil (780 tons), while the soil BDE-209 inventory (44 tons) was considerably smaller. On the other hand, current use of large amounts of BDE-209 in numerous commercial products has resulted in a much higher atmospheric depositional flux of BDE-209 (28.1 tons/yr) relative to that of *p,p'*-DDT (0.31 tons/yr). The soil inventory of *p,p'*-DDT is predicted to decrease to half of its current value after 22 years, and the percent area containing soil *p,p'*-DDT at levels exceeding the effects range-medium (27 ng/g) will decrease from 40% to 20%. In addition, soil BDE-209 inventory will reach an equilibrium value of 940 tons in ~60 years, when BDE-209 levels in 50% of soil will be above an equivalent risk guideline value (125 ng/g).

In another case study, sediment samples were collected in 2008 from a highly urbanized river basin within the PRD and analyzed for polycyclic aromatic hydrocarbons (PAHs). Source diagnostics suggested that sediment PAHs stemmed mainly from coal combustion, refined fossil fuel combustion and oil spills, accounting for 37%, 32% and 23%, respectively, of the total loading. Further analyses of energy consumption patterns in the region indicated that the amounts of fossil fuels consumed between 2002 and 2008 had doubled, but the sediment PAH levels during the same time period had remained largely unchanged. This was attributed to improved fuel consumption efficiency stemming from a combination of reduced use of coal for power generation, adoption of better technology such as coal gasification, and more stringent standards on automobile emissions.

To assess dietary intake of DDTs (sum of *o,p'*- and *p,p'*-DDT, DDD and DDE) and polybrominated diphenyl ethers (PBDEs) for local residents due to seafood consumption, a total of 602 seafood samples, including fish, shrimps, crabs and molluscs, were collected and analyzed. Based on the residual levels of DDTs and PBDEs and a recent dietary survey at the same sampling locations, dietary intakes of DDTs and PBDEs by local residents via

seafood consumption for all age groups were estimated to be 147–564 ng/day and 4.7–18.5 ng/day, or 8.5–12.9 ng/kg bw/day and 0.27–0.46 ng/kg bw/day, respectively. Among the different seafood types, fish contributed the largest portion of the dietary intakes of DDTs (57%), followed by molluscs (38%). Similarly, the dietary intakes of PBDEs were also dominated by fish (45%) and molluscs (45%). Assessment based on several available guidelines suggested that though no significant human health risk associated with the dietary intake of PBDEs, a lifetime cancer risk from dietary exposure to DDTs remains a probability. Because dietary intake of DDTs was dominated by fish and molluscs, added concern should be paid to fish and molluscs.

ECOLOGICAL STUDY OF REVEGETATED COAL MINE SPOIL OF AN INDIAN DRY TROPICAL ECOSYSTEM ALONG AN AGE GRADIENT

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INTRODUCTION

In India, open pit coal mining constitutes 81 per cent of the total coal extraction resulting substantial removal of undesirable waste materials in the form of mine spoil dumps. The immediate effect is the destruction of existing vegetation-soil-geology circuit and also the plant and soil biomass. Mine spoils are devoid of soil nutrients, organic matter, soil microbes and unfavorable physico-chemical conditions. Consequently spoils are not conducive for early plant succession and microbial growth. These are characterized by either very coarse texture with low water retention capacity, or very high bulk density, resulting in poor drainage along with slope instability and sparse cohesion, therefore, mine spoils are prone to landslides, water and air erosion. *In situ* management of such damaged coal-mine lands is an enormous, multiplicative and challenging issue throughout the globe.

A long term study was conducted to understand the impact of revegetation on the changes of soil mineral nitrogen (N), N-mineralization rate, soil microbial biomass N (MBN) and below ground root biomass (BGB) and factor of safety status of mine spoil after 2, 6, 10 and 12 yrs of mine spoil revegetation.

METHODS

Three sites comprising of revegetated, non revegetated coal mine spoils, and adjacent dry tropical forest of Dhanbad coalfields, Jharkhand state of India, were selected to quantify the mineral N (nitrate- and ammonium-N) content, soil N-mineralization, MBN and BGB at intervals of 2, 6, 10 and 12 yrs of revegetation. Nitrate-N and ammonium-N were determined by the phenol-di-sulphonic acid (Jackson, 1985), and phenate methods (Wetzel and Likens, 1979), respectively. Soil nitrogen mineralization was quantified by field incubation (Pastor, et al., 1984) and MBN by chloroform fumigation extraction methods (Brookes et al., 1985). Belowground biomass (live + dead root) was measured by monoliths of 15X15X10 cm size in each site. Statistical analysis was performed using SPSS Base 7.5 (1997).

RESULTS AND DISCUSSION

Mineral N ranged from 1.89-6.34 $\mu\text{g/g}$, net mineralization from 1.06-25.2 $\mu\text{g/g/mo}$, MBN from 6.2-71.2 $\mu\text{g/g}$ and BGB from 19.2 to 575 gm^{-2} . Revegetation increased the mineral N by 8, 11.3, 26.7 and 28.94%, BGB by 43, 86.6, 91 and 94%, N-mineralization by 43, 80, 91.6 and 92.34% and MBN by 37.8, 52.37, 65.8 and 72.51% after 2, 6, 10 and 12 yrs, respectively. The gradual increase may be due to increase in leaf litter fall, root decay, fixation of atmospheric N leading to increase in microbial biomass and N-mineralization rate from the added organic matter. Role of soil fauna and bird droppings may also not be ruled out. According to Sharma and Sunderraj (2005), the natural recovery takes much longer time through colonization of plant and animal species. Singh and Singh (2006) reported that restoration helps to restore the soil fertility and enhances biological diversity. MBN was positively ($P < 0.05$) related to BGB and the revegetation age. BGB was positively ($P < 0.05$) related to total soil N (TSN).

Contours of Mohr-Colomb factor of safety (FOS) drawn for the dump with and without revegetation at ages of 3 and 12 years have shown that FOS was enhanced from 1.4 to 1.8 and 2.2, respectively due to root growth on the dump. This is because of the mechanical action of the tree and grass roots, which reinforces the dump material by roots and enhances the shear strength of the dump material (Chaulya et al., 2000). Therefore, binding of the

dump surface with vegetation and increase in shear strength lead to an enhanced factor of safety at mine spoil depth.

Table 1: Mineral N, below ground biomass, N-mineralization rate and soil microbial biomass N in forest, mine spoils and revegetated mine spoils.

Year	Parameters	Forest	Mine spoils	Revegetated Mine spoils
2 yrs.	Mineral-N ($\mu\text{g/g}$)	6.34 \pm 0.7	1.89 \pm 0.14	2.06 \pm 0.23
6 yrs.		6.34 \pm 0.7	1.89 \pm 0.14	2.13 \pm 0.25
10 yrs.		6.34 \pm 0.7	1.89 \pm 0.14	2.58 \pm 0.18
12 yrs.		6.34 \pm 0.7	1.89 \pm 0.14	2.66 \pm 0.24
2 yrs.	Belowground biomass (gm^2)	556 \pm 12.4	19.2 \pm 1.4	33.8 \pm 7
6 yrs.		561 \pm 13.8	19.6 \pm 1.4	147 \pm 12
10 yrs.		572 \pm 19	19.6 \pm 1.4	214 \pm 12
12 yrs.		575 \pm 18	19.8 \pm 1.4	338 \pm 2.4
2 yrs.	N-mineralization ($\mu\text{g/g/mo}$)	17.5 \pm 1.4	1.06 \pm 0.14	1.87 \pm 0.2
6 yrs.		20.4 \pm 1.3	1.06 \pm 0.14	5.45 \pm 0.28
10 yrs.		23.8 \pm 1.7	1.06 \pm 0.14	12 \pm 0.45
12 yrs.		25.2 \pm 1.3	1.06 \pm 0.14	13.85 \pm 0.76
2 yrs.	Microbial biomass N ($\mu\text{g/g}$)	69.6 \pm 5.5	6.22 \pm 0.5	10 \pm 0.8
6 yrs.		70.2 \pm 5.0	6.22 \pm 0.5	13.06 \pm 1.0
10 yrs.		70.8 \pm 5.5	6.22 \pm 0.5	18.2 \pm 1.5
12 yrs.		71.2 \pm 6.0	6.22 \pm 0.5	22.63 \pm 2.0

CONCLUSION

Revegetation increases the soil organic matter along with BGB, mineral soil nutrient, nitrogen transformation rates and microbial biomass. The revegetation age has a major contribution in enhancing soil fertility and soil redevelopment of the mine spoil. These positive attributes are important for socio-economic development. Therefore, revegetation can be considered as a management tool for the sustainable development of the Indian mining industries.

Acknowledgements: Funding supports from Dept. of Science & Technology & CSIR, New Delhi

REFERENCES

- Brookes, P.C., Landman, A., Pruden, G. and Jenkinson, D.S. (1985) Chloroform fumigation and release of soil N: A rapid direct extraction method to measure microbial biomass N in soil. *Soil Biol. Biochem.* 17: 837-842.
- Chaulya, S.K. Singh, R.S. Chakraborty, M.K. and Tewary, B.K. (2000). Bioreclamation of coal mine overburden dumps in India. *Land Contamination & Reclamation*, 8(3), 189-199.
- Jackson, M.L. (1958) *Soil Chem Anal.* Prentice Hall, Englewood Cliffs.
- Pastor, J., Aber, J.D., McClaugherty, C.A. and Melillo, J.M. (1984) Above ground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. *Ecology*, 65: 256-268
- Sharma, D. and Sunderraj, S.F.W. (2005). Species selection for improving disturbed habitats in Western India, *Current Science*, 88 (3), 462-467
- Singh, A. N. and Singh, J.S. (2006). Experiments on ecological restoration of coalmine spoil using native trees in a dry tropical environment, India: a synthesis, *New Forests*, 31, 25-39
- SPSS (1997) SPSS Base 7.5 Application Guide. SPSS Inc., Chicago
- Mays, D.A. and Bengston, G.W. (1978) In: Schaller, F.W., Sutton, P. (Eds.), Reclamation of drastically disturbed lands. *American Society of Agronomy*, Madison, WI, 307-327
- Wetzel, R.G. and Likens, G.E. (1979) *Limnological Analyses*, 357. W.B. Saunders Co. Philadelphia

THE PHYTOAVAILABILITY OF COPPER AS AFFECTED BY BIOSOLIDS-BASED CO-COMPOSTED PRODUCTS

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INTRODUCTION

The mobilization of heavy metals in contaminated soils for plant uptake and leaching to groundwater can be minimized by reducing the bioavailability of metals through chemical and biological immobilization (Naidu *et al.*, 2008). Currently, there has been increasing interest in the immobilization of heavy metals using a range of inorganic compounds, such as lime, alkaline waste materials as well as organic by-products, such as 'exceptional quality' alkaline biosolids (Haynes *et al.*, 2009; Bolan *et al.*, 2011). Immobilization techniques to remediate metal contaminated soils has been used widely in several countries including Australia and New Zealand. While biosolids have been proven to be efficient in the reclamation of former mining sites and landfill sites by reducing the bioavailability of heavy metals *in situ* (Brown *et al.*, 2004). However, adding biosolids-based co-composted products for mine revegetation may cause soluble dissolved organic carbon (DOC)-metal complexes to form, thereby affecting the phytoavailability of metals. Therefore this study is to investigate the effect of biosolids-based co-composted products (co-composted with lime, red mud and bentonite) on the phytoavailability of Cu in mine soil using Indian mustard (*Brassica juncea* L.).

METHODS

Biosolid sample was collected from the Bolivar Wastewater Treatment Plant in South Australia. It was air dried and sieved to < 2 mm using a stainless steel sieve and then biosolids was mixed with lime at 5% w/w basis, red mud or bentonite at 20% w/w basis. All samples were wetted to 70% of the water holding capacity (WHC) and were incubated under aerobic conditions at room temperature for three months before applying to tested soils. Naturally contaminated mine soil (< 20 cm depth) with a Cu concentration of 1820 mg kg⁻¹ was collected from an abandoned Cu mine at Kapunda, South Australia. The soil sample was mixed with biosolids alone, biosolids blended with lime, red mud and bentonite at 10% w/w basis (i.e. 200Mg ha⁻¹). All samples were wetted to 70% of the WHC and incubated under aerobic condition for 3 months before using for pot experiments. For the plant growth experiment, the modified method of Stanford and Dement was used in this work. Round transparent plastic pots of 700 ml capacity with bottoms removed were nested in similar containers with bottom intact and filled with 500 g of sand. Approximately 12-15 seeds of mustard were sown directly into the sand at a depth of 5 mm and Cu-free nutrient solution was added to each pot twice a day to the required moisture content. The plants were thinned to 7 seedlings per pot after two weeks. After 6 weeks of plant growth, the plastic containers containing plants were transferred to plastic containers holding 100 g of Cu mine soil, thus placing the dense mat of roots (Fig. 1A) in intimate contact with the soil. The soils were wetted to 70% WHC before the transfer of plant containing pots. Moisture losses were replenished with periodic water/nutrient solution additions. Plants were harvested at 10 weeks after sowing.

RESULTS AND DISCUSSION

The pH of the mine soil with and without co-composted products increased following the plant growth experiment. The NH₄NO₃ extractable concentration of Cu (Cu_{NN}), which

represents potentially bioavailable Cu was lower in soil sample mixed with all co-composted products and biosolids alone than control soils at the end of the plant experiments. For plant experiments, it was clear that amendment application had a significant effect on both root and shoot dry weights and all amendment applications increased the dry matter yield in mine soil (Fig. 1B). Application of all amendments in soil decreased the root and shoot Cu concentration in Indian mustard and biosolids blended with lime reduced the Cu concentration in plant tissues more than the other amendments (Fig. 1C). Adding amendments increased organically bound fractions and reduced exchangeable fractions of Cu in soil. Application of biosolids blended with lime increased the percentage of carbonate bound Cu in soils more than the other biosolids-based co-composted products. Biosolids blended with red mud increased the percentage of Mn/Fe oxyhydroxide bound Cu in soils more than biosolids alone and biosolids blended with lime and bentonite.

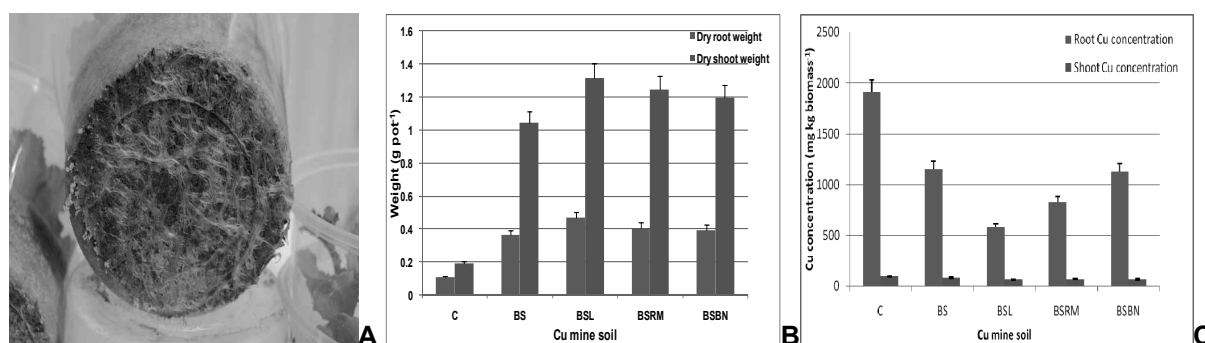


Fig.1 (A) Plant root mat, (B) plant dry weights and (C) Cu uptake in plants in Cu mine soil (C; control) in the presence of biosolids alone (BS) and biosolids blended with lime (BSL), red mud (BSRM) and bentonite (BSBN) after plant experiments. Error bars indicate the standard deviation between replicates.

CONCLUSIONS

The application of all amendments on mine soil increased soil pH and reduced NH_4NO_3 extractable Cu (Cu_{NN}) in soil samples after plant experiments. Application of biosolids blended with lime resulted in the highest soil pH and the lowest Cu (Cu_{NN}) concentration in soil samples. Addition of amendments proved to be effective in increasing plant root and shoot yields in mine soil. Biosolids-based co-composted products reduced Cu concentration in plant root and shoot tissues and biosolids blended with lime reduced the Cu concentration in plant tissues more than the other amendments.

REFERENCES

- Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, T., McDowell, R. and Senesi, N. (2011). Dissolved organic matter: biogeochemistry, dynamics and environmental significance in soils. *Advances in Agronomy*. **110**, 1-75.
- Brown, S., Chaney, R., Judith, H., James, A.R. and Willam, R.B. (2004). In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium. *Journal of Environmental Quality*. **33**, 522-531.
- Haynes, R.J., Murtaza, G. and Naidu, R. (2009). Chapter 4 Inorganic and organic constituents and contaminants of biosolids: Implications for land application. *Advances in Agronomy*. **104**, 165-267.
- Naidu, R., Pollard, S.J.T., Bolan, N.S., Owens, G. and Pruszinski, A.W. (2008). Bioavailability: The underlying basis for risk-based land management. *In Chemical Bioavailability in Terrestrial Environments*. (R. Naidu, Eds.), pp. 53-72. ELSEVIER, UK.
- Stanford, G. and Dement, J.D. (1957). A method for measuring short-term nutrient absorption by plants: 1. Phosphorus. *Soil Science Society of America Proceedings*. **21**, 612-617.

ACCOUNTING FOR CHEMICAL SATURATION AND SOLUBILITY LIMITS IN THE DERIVATION OF SITE SPECIFIC REMEDIATION CRITERIA

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INTRODUCTION

The derivation of site specific remediation criteria (SSRC) in Australia generally follows published methodology (NEPM (1999) and Enhealth (2004), USEPA (1994)), to determine media specific chemical concentrations which are protective of human health.

In determining SSRCs, chemical properties for pure chemicals are adopted in order to derive a safe exposure level which is protective of human health for all relevant pathways. As this approach is based on the theoretical chemical properties of pure chemical it does not take into account the effect of chemical mixtures and the impact on chemical properties such as saturation and solubility limits.

The derivation of SSRCs needs to be based on a level of acceptable chemical concentration in the environmental media which has considered solubility and saturation limits (based on theoretically published values for either the chemical or an appropriate surrogate). If solubility and saturation limits are not considered in the determination of SSRCs, there is the potential to derive levels which are equivalent of separated phase concentrations, which will not be accepted by regulators. However there are limitations in adopting theoretical solubility and saturation limits in the determination of SSRCs as these are based on pure chemicals in a laboratory environment and they are not representative of actual solubility or saturation limits observed in the field.

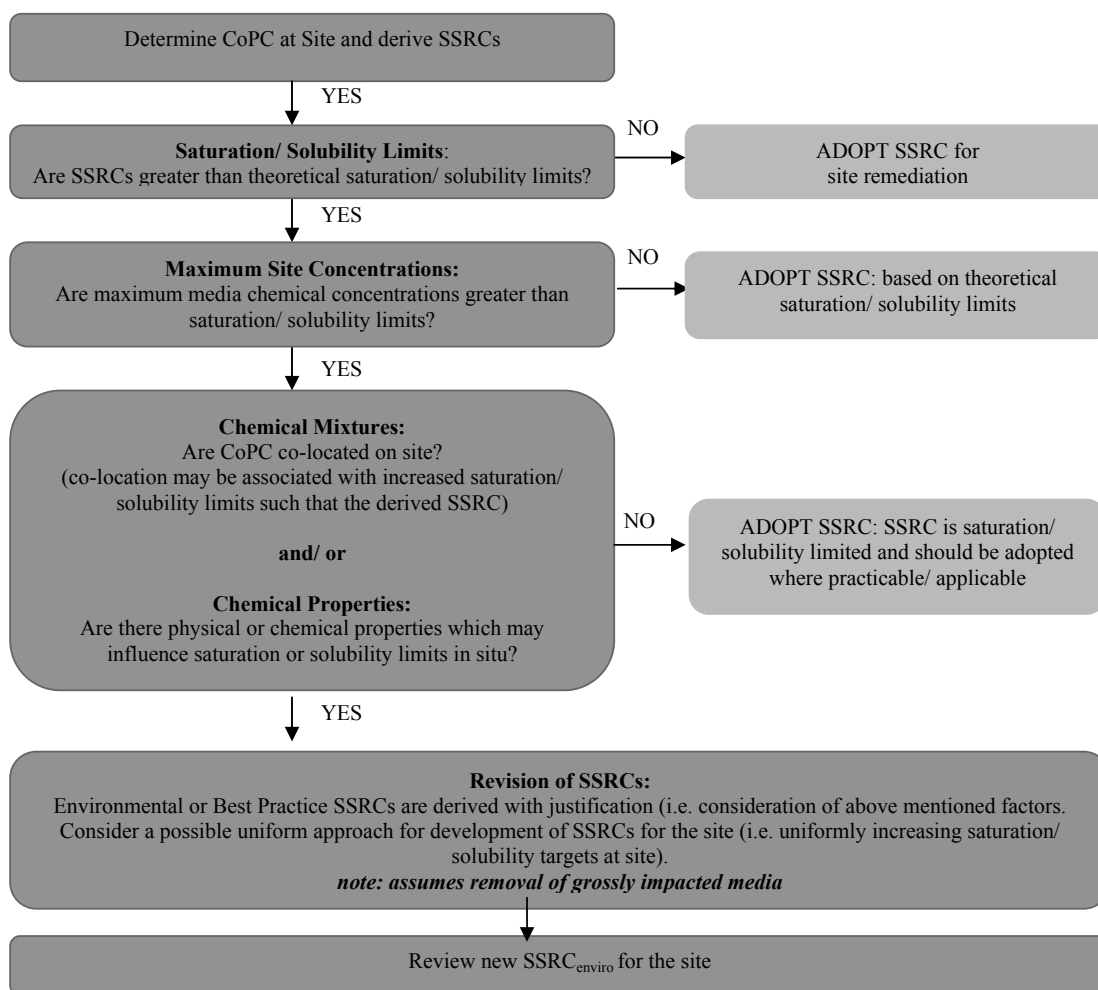
Industrial site remediation programs often involve multiple chemicals co-located in environmental media which will affect a number of physical and chemical properties such as solubility and saturation limits.

Soil and groundwater monitoring data from locations where chemical mixtures have been detected usually indicates that the actual dissolved phase and unsaturated soil concentrations may be numerous orders of magnitude greater than the theoretical saturation or solubility limits. This suggests some limitations to the application of theoretical chemical properties in the derivation of SSRCs for situations where chemicals are collocated, and limits the usefulness of the derived SSRCs in practical reality.

In order to overcome this dilemma, AECOM have come up with a number of additional considerations for risk assessors to consider when deriving SSRCs for remediation purposes.

APPROACH TO DERIVATION OF REALISTIC SSTCS

The following diagram outlines the approach adopted by AECOM:



CONCLUSIONS

AECOM have developed a systematic approach to the derivation of SSTCs which are (1) practical, based on multiple site specific considerations and are (2) environmentally sustainable (i.e. are not based on theoretical published limits which will warrant excessive remediation).

Determining SSRCS based on environmental goals where theoretical solubility/ saturation limits apply, enables consultants, regulators and clients monitor, measure and achieve remediation goals

REFERENCES

- enHealth (2004). *Environmental Health Risk Assessment, Guidelines for Assessing Human Health Risks from Environmental Hazards*. June 2004.
- National Environment Protection Council (1999a). *National Environmental Protection (Assessment of Site Contamination) Measure, Schedule B(4), Guideline on Health Risk Assessment Methodology*.
- National Environment Protection Council (1999b). *National Environmental Protection (Assessment of Site Contamination) Measure, Schedule B(7), Guideline on Health-Based Investigation Levels*.
- USEPA 1994, *Air Emissions Models for Waste and Wastewater*, EPA-453/R-94-080A (1994).
- USEPA, 2004a. *User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings*. United States Environmental Protection Agency, Office of Emergency and Remedial Response. Revised February 22, 2004.

RISK ASSESSMENT OF HEAVY METALS AND METALLOIDS FROM HISTORICAL MINE PRACTICES IN THE LEICHHARDT RIVER AND SURROUNDING LOCATIONS

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INTRODUCTION

A health risk assessment was undertaken at Mount Isa to assess metal or metalloid including lead contamination of the Leichhardt River, of residual contamination from mine sediments largely resulting from mine practices in the 1940s, and at the town swimming pool/ Kruttschnitt oval area (Noller et al. 2009). The National Environment Protection Measure (NEPM) guidelines give advice on how to deal with soil contamination in Australia and further assessment is required by the NEPM if the Health Investigation Levels (HIL) are exceeded (NEPC 1999). In the absence of site specific bioavailability data, it is usually assumed to be 100% for risk assessment purposes. It is not uncommon that elevated metal or metalloid concentrations such as lead, arsenic and cadmium in contaminated samples exceed these HIL values which could have adverse health implications. It has also been identified that the current NEPM do not provide accurate close out criteria for mined land as the bioavailability of contaminated soil is usually a fraction of 100%. For health risk assessment purposes bioavailability (BA in-vivo) is the amount of a contaminant that is absorbed into the body following skin contact, ingestion, or inhalation; bioaccessibility (BAc in-vitro) is the fraction of the total concentration that has the potential to be absorbed into the human body as estimated by simulation of the gastro-intestinal tract. A review of currently used bioavailability and bioaccessibility methods and limitations gives general guidance in the NEPM for determining their use and application in contaminant site assessment and as a guidance for mining industry (Ng et al. 2010). A practical approach to predict bioavailability uses in-vitro PBET (physiologically based extraction test) to determine the bioaccessibility of individual soils (Bruce et al. 2007; Ruby et al. 1996).

METHODS

Mine waste samples can be tested for bioaccessibility (PBET) under various pHs in a synthetic gastric fluid system. pH values that apply are 1.3, 2.5 and 4.0 simulating fasting, partially fed and fed stomach conditions respectively, and at pH 7.0 simulating the small intestinal pH condition. The study used targeted sampling at 21 locations to: (i) Determine the distribution of contamination within an area known to be previously contaminated; (ii) Calculate the bioaccessible (BAc) fraction of total heavy metals and arsenic using a PBET method (Bruce et al. 2007); and (iii) Complete a desktop human health risk assessment to estimate the site-specific potential toxicity of lead and arsenic (Noller et al. 2009).

RESULTS AND DISCUSSION

The first step in the human health risk assessment for soils in the Leichhardt River was to compare the total concentrations of heavy metals and arsenic against the National Environmental Protection Measure (NEPM) Health Investigation Level (HIL) Level E (NEPC, 1999). The Level E Health Investigation Level applies to parks, recreational open space and playing fields. Residential sites were not a part of this study. This comparison of concentrations in soil assumed 100% bioavailability and initially showed that exceedances occurred at a number of sites for arsenic, cadmium, cobalt, copper, lead and zinc. Sites at the swimming pool and the Leichhardt River downstream were below the HIL Level E concentration and did not show evidence of contamination. According to the National

Environmental Protection Council (NEPC) risk assessment process, exceedances of the HILs trigger the requirement to undertake a Tier II risk assessment including toxicity assessment. Hence bioaccessibility, used to predict bioavailability, was calculated for each of the sites to allow for site specific risk assessment. The values of the key contaminants were adjusted for bioaccessibility and compared, once again, with the NEPM HIL Level E criteria. After bioaccessibility was taken into account fewer metals/metalloids were of concern and the number of sites considered to be contaminated with respect to human health was reduced. The area of known contamination, in the river between Grace Street Bridge and downstream of the Velodrome continued to show exceedances of the NEPM HIL Level E criteria for lead, copper, cadmium and zinc. Copper was also still in exceedance of the criteria at the Death Adder Gully sites.

The significance of lead and arsenic in soil to human health was assessed by conducting a desktop human health risk assessment that examined both acute and chronic effects. It determined that: (i) Contaminated soils, as sampled in this study, are unlikely to cause acute or sub chronic lead or arsenic toxicity; (ii) Chronic lead toxicity is unlikely to occur in adults; (iii) In a residential scenario, elevated concentrations of lead in soil combined with high bioavailability (i.e. soils with concentrations of >1,200 mg/kg with a bioavailability of >20% or concentrations >2,400 mg/kg with bioavailability of >10%) do have the potential to cause chronic lead toxicity in children. It must be noted that related studies have shown that lead bioavailability is generally much lower than bioaccessibility as used to predict bioavailability in this study. Risk is reduced even further in recreational areas as the exposure time is greatly decreased; arsenic in soil is unlikely to cause chronic toxicity in humans because people are unlikely to ingest sufficient amounts of soil under normal circumstances.

CONCLUSIONS

The findings presented in this study resulted in further remediation work to remove historical mine sediments within the Leichhardt River. The Leichhardt River Remediation Project was completed in May 2008. Given the findings and observations from this initial study future investigations should include: (i) completion of a more detailed study of bioavailability of heavy metals, particularly lead, using animal uptake studies to give a reliable and more refined human health risk assessment and (ii) verification of the predictive potential of the bioaccessibility technique for bioavailability; and (iii) further development of knowledge on heavy metal pathways that may have the potential to impact on human health.

ACKNOWLEDGEMENT

The project was funded by Mount Isa Mines Ltd, Xstrata Copper.

REFERENCES

- Bruce, S. Noller, B., Matanitobua, V. and Ng, J. (2007) In Vitro Physiologically-based Extraction test (PBET) and Bioaccessibility of Arsenic and lead from Various Mine Waste Materials. *Journal of Toxicology and Environmental Health, Part A* 70 1700-1711.
- Ng, J.C, Juhasz, A.L., Smith, E., and Naidu, R. (2010). Contaminant bioavailability and bioaccessibility. Part 1: A scientific and technical review. and Part 2: guidance of industry. *CRC CARE Technical Report No. 14*, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
- Noller B, Matanitobua V, Ng J (2009). Study of Heavy Metals and Metalloids in the Leichhardt River and Surrounding Locations. *Lead Pathways Study - Phase 1* (Emissions to Land) <http://www.xstrata.com/operation/mountisa/publications/>
- NEPC (1999) *National Environmental Protection* (Assessment of Site Contamination) *Measures*, National Environment Protection Council, Adelaide.
- Ruby, M. V., Davis, A., Schoof, R., Eberle, S. and Sellstone, C.M. (1996). Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environmental Science and Technology* 30(2): 422-430.

RISK APPROACH TO GROUNDWATER REMEDIATION – LONDON CASE STUDY

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INTRODUCTION

Ten areas requiring groundwater remediation were identified as part of the redevelopment of a large Brownfield site in London.

A site specific remedial strategy (SSRS) was undertaken for each individual area, where remedial targets for the contaminants of concern were calculated using a risk-based approach. Inputs into the risk assessment included the location and condition of the final receptor, the migration pathway, the mobility and degradation of the contaminant and the extent to which the source of contamination has been removed. A site wide groundwater model was also used to determine the future groundwater gradients subsequent to the impending impoundment of the waterway.

AREA 1

In one area, dual phase vacuum extraction (DPVE) was used to remove light non aqueous phase liquid (LNAPL) from the shallow aquifer. Over 520L of LNAPL was removed from the aquifer, however measurable LNAPL was still present in a small source area and recovery efficiency had decreased with time. The pathway to the “Controlled Waters” receptor was elongated by the construction of a cut off wall and the risk assessment was revised to take into consideration the revised input parameters. The revised risk assessment was able to demonstrate that the DPVE could be decommissioned and no further remediation was required based on the low risk posed by the residual LNAPL.

AREA 2

In a separate area, a chlorinated solvent plume was observed to have migrated both laterally and vertically from the source of the contamination. The initial SSRS produced remedial targets in the source area that were not practical to achieve. A hydraulic containment system was initially installed to prevent the continuation of lateral migration of the contaminants away from the source. A number of detailed investigations were undertaken to fully characterise and delineate the plume, which resulted in a continually improved conceptual site model (CSM). With the updated CSM approved by the regulators, a risk assessment was undertaken to determine what concentrations would be acceptable within the source area that would not result in expansion of the plume or further degradation of the aquifer. ISCO was considered a sustainable solution to achieve the residual source area target concentrations. Results have indicated up to 99% reduction in contaminant concentrations six months post injection. The regulator has agreed to the decommissioning of the hydraulic containment system, bringing forward the scheduled end of active remediation and saving the client money.

OTHER AREAS

Other areas where risk assessment has been used to assist in the final remedial goal will also be presented.

CONCLUSIONS

Active remediation has now ceased across the Site with only verification monitoring remaining. The combination of an integrated risk based approach to both soil and

groundwater remediation, along with the close involvement of the regulators, has allowed the client to complete groundwater remediation ahead of schedule and has reduced the projected overall lifespan costs of groundwater remediation at the site.

ARE CURRENT AND PROPOSED ASBESTOS IN SOIL GUIDELINES PROTECTIVE OF HUMAN HEALTH?

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INTRODUCTION

Australia and many other countries are developing or improving guidance for dealing with asbestos-contaminated soils. There is an increasing amount of information available on the toxicology and epidemiology of asbestos exposure as well as more sophisticated approaches to occupational and public health monitoring, waste management, and regulation of bonded and friable asbestos products. This new information needs to be synthesized to achieve a consistent approach to risk assessment across the various guidance documents.

In comparison to countries such as the United States, United Kingdom, and the Netherlands, until only recently Australia has developed little guidance in contaminated site clean-up of asbestos. While the challenge of developing a methodology that is protective of human health, scientifically-defensible and is accepted on a national basis is daunting, Western Australia (WA) has recently made progress in introducing thresholds for soil and air concentrations of asbestos for contaminated land sites. Soon to follow are national guidelines proposing similar assessment criteria currently in draft form. However, for these guidelines to be implemented fully, Australia requires social and political acceptance of a 'safe' asbestos exposure level that is deemed protective of human health.

ASSESSMENT METHODS AVAILABLE

Australia

In Australia, risk assessors are now able to assess risk at asbestos-contaminated soil sites using the *Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia* and the soon-to-be-released *National Environmental Protection (Assessment of Site Contamination) Measure (NEPM)*. Both guidance documents provide a framework whereby the appropriate risk management methodology, and if required, remediation end point, can be determined for different land uses and different forms of asbestos contamination (bonded and friable/free fibre contamination). Criteria contained within these guidelines have been derived from research completed in the Netherlands, with additional safety factors included to take into account drier Australian conditions and treatment of mineralogical forms of asbestos as equivalent.

Of critical importance is the differentiation between the form of contamination and the site's proposed end use. WA Guidelines specify a soil threshold of 0.001% (w/w) for fibrous asbestos or asbestos fines where a factor of safety of 10 was applied to the Netherlands threshold of 0.01% (w/w). If extrapolating measured field data obtained to develop the Netherlands Standard NEN5707 to determine an air concentration of asbestos resulting from a soil concentration of 0.001% (w/w), data indicates an air concentration within the range 0.000005 f/mL to 0.00005 f/mL would be generated. With reference to the World Health Organisation (WHO) Guidelines, and as referenced in the WA Guidelines, an air concentration of 0.0001 f/mL corresponds to a lifetime cancer risk of 10^{-5} to 10^{-6} , a range broadly accepted by the WA Department of Health.

Netherlands

In 2010, the Health Council of the Netherlands proposed revised thresholds for ambient air concentrations of asbestos. Health risks have been re-evaluated with a proposed reduction in air thresholds contained within NEN5707. Currently a weighted air concentration based on fibre type and length of 0.001 f/mL is associated with 10^{-6} lifetime cancer risk level. The current soil threshold with reference to NEN5707 is 0.01% (w/w) weighted for friable asbestos. If the air thresholds shown in Table 1 are implemented into policy, the soil threshold value for friable asbestos may be reduced.

Table 1. Proposed air thresholds for asbestos by the Health Council of the Netherlands.

Lifetime Cancer Risk	Air Threshold Based on Fibre Type (f/mL)		
	Combination (up to 20% amphibole)	Serpentine	Amphibole
10^{-4}	0.0013	0.0028	0.0003
10^{-5*}	0.00013	0.00028	0.00003
10^{-6}	0.000013	0.000028	0.000003

* 10^{-5} lifetime cancer risk linearly extrapolated between 10^{-4} and 10^{-6}

DISCUSSION

With respect to the proposed new ambient air asbestos thresholds in the Netherlands, WA Guidelines and the soon-to-follow updated NEPM may not be as conservative as once believed. Previous studies completed in the Netherlands and the United Kingdom have shown a relationship between soil moisture content and the ability for fibre generation. As Australia would typically experience drier conditions compared to the Netherlands, one would expect soil thresholds in Australia to be more conservative to account for drier environmental conditions and the ability for a greater amount of asbestos to enter the exposure-pathway.

When comparing the proposed Netherlands air threshold range for a combination of serpentine and amphibole fibre types (up to 20%) and the WA Guidelines for a lifetime cancer risk range of 10^{-5} to 10^{-6} , air concentrations are comparable (i.e. 0.00013 f/mL to 0.000013 f/mL in the Netherlands compared to 0.0001 f/mL in WA). For the same lifetime cancer risk range, WA Guidelines slightly exceed the proposed Netherlands thresholds when purely amphibole contamination is present. Although WA Guidelines have used soil criteria contained in NEN5707 as a basis for developing similar criteria, WA Guidelines reference the WHO air criteria and do not differentiate between amphibole and serpentine fibre types. Therefore, the relationship between soil and air concentrations of asbestos is the key, with the ability for a certain air concentration to be generated from a specified soil contamination level. Based on Netherlands data a soil contamination level of 0.001% (w/w) for fibrous asbestos or free fibre is appropriate as less than 0.0001 f/mL asbestos can be generated.

REFERENCES

- enHealth Council (2005). *Management of Asbestos in the Non-Occupational Environment*. Australian Government, Department of Health and Aging and enHealth Council, Australia.
- Health Council of the Netherlands (2010). *Asbest (English translation – Asbestos)*. Health Council of the Netherlands, Netherlands.
- National Environment Protection Council (2011). *National Environmental Protection (Assessment of Site Contamination) Measure: Draft Schedule B1 – Guideline on Investigation Levels for Soil and Groundwater*. National Environment Protection Council Service Corporation.
- Tempelman J, Tromp PC, Swartjes FA, Knol AB (2010). *Praktische consequenties van het advies van de Gezondheidsraad inzake asbest 2010 (English translation – Consequences of the Advice on the Health of Asbestos 2010)*. Netherlands Organisation for Applied Research, Bilthoven.
- Standards Australia (2004). *Australian Standard 4964 – Methods for the qualitative identification of asbestos in bulk samples*. Standards Australia.
- Western Australia Department of Health (2009). *Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia*. Western Australia Department of Health Australia.

ASBESTOS IN AIR AND SOIL

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INTRODUCTION

Current guidelines for assessing asbestos in soil are designed primarily to address the dominant problem of asbestos cement fragment contaminated soil (WA-DOH, 2009). Proposed variations to the site contamination National Environment Protection Measure refer to these guidelines. Free asbestos fibre in soil and long-term exposures to low levels of asbestos in air are areas where conventional practices may be inadequate to protect public health. Similarly, low level exposures for children can drive lifetime risk for an asbestos disease to unacceptable levels.

The political question is - what is an acceptable level of risk for the public? The scientific questions relate to quantifying and managing risk and these matters can generate somewhat unnecessary dispute. The key appears to be identifying high-priority risk scenarios and then managing the high priority scenarios.

The USEPA asbestos risk based concentration calculator is a useful management tool (USEPA, 2008). Whether the risk levels determined are valid is one question, however the ability to compare and prioritise risk scenarios would appear to be the greatest value of this tool. Its use related to asbestos in air and asbestos in soil are assessed.

METHODS

The USEPA risk based concentration calculator is used to generate a graph that can be used in assessing and prioritising risk scenarios and to decide what asbestos in air concentrations or detection limits may be appropriate in any given situation. Given this framework, asbestos in soil to asbestos in air transfer experiments from Scotland (Addison *et al.*, 1988) are evaluated with a view to assessing criteria for asbestos in soil, and measurement of asbestos in soil.

RESULTS AND DISCUSSION

Graphs that use life time exposures as well as 12 month duration exposures are useful tools in assessing high priority settings (Figure 1 lifetime exposure scenarios). The Addison experiment (Figure 2) appears to have been tailored for occupational risk scenarios and not public health risk. Suggestions are made in relation to required experiments and techniques to evaluate asbestos in soil risk for free fibre.

REFERENCES

- Addison, J., Davies, L. S. T., Robertson, A., Willey, R. J., The release of dispersed asbestos fibres from soils. Technical Memoranda, TM/88/14. Institute of Occupational Medicine, 1988, pp. 50.
- USEPA, 2008. Asbestos RBC Calculator (MS Excel). USEPA
http://www.epa.gov/superfund/health/contaminants/asbestos/compendium/risk_assessment.html accessed April 15th 2011.
- WA-DOH, 2009. Guidelines for the Assessment, Remediation and Management of Asbestos-Contaminated Sites in Western Australia. Western Australian Department of Health accessed at http://www.public.health.wa.gov.au/2/656/2/contaminated_sites.pm 25th November 2009, Perth.

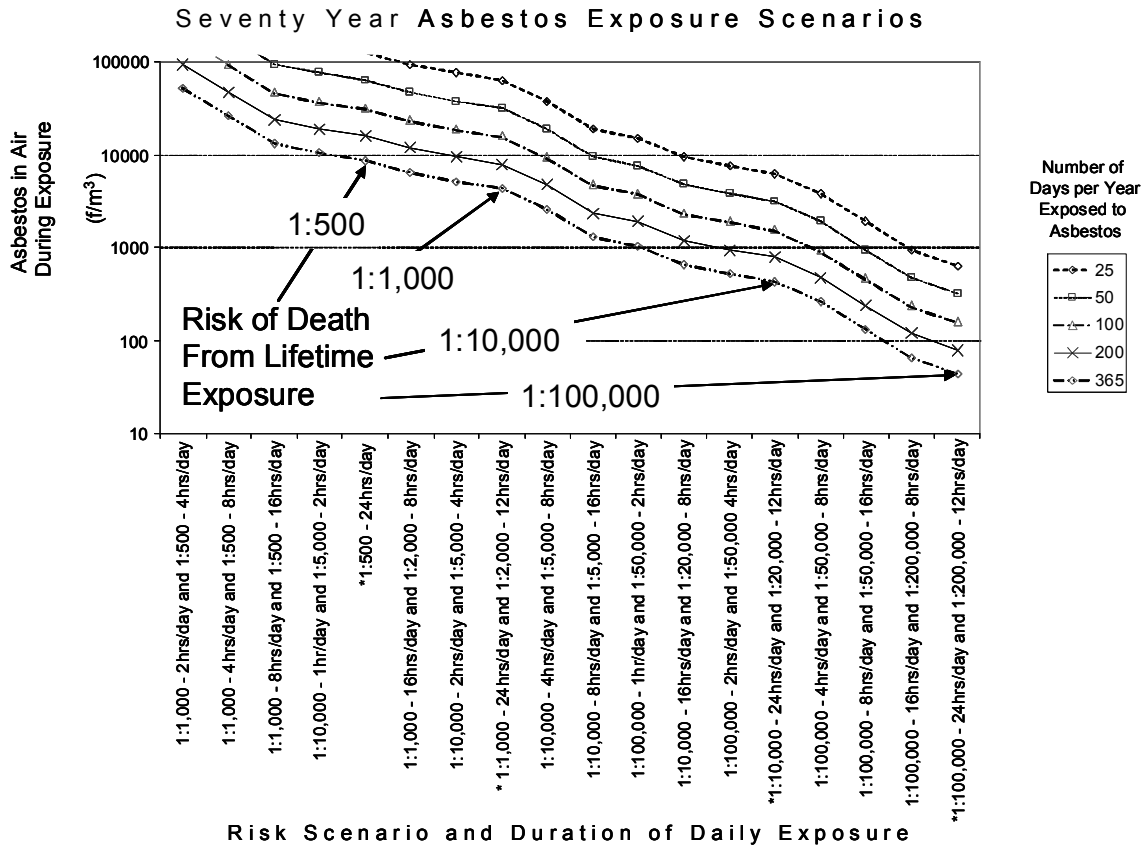
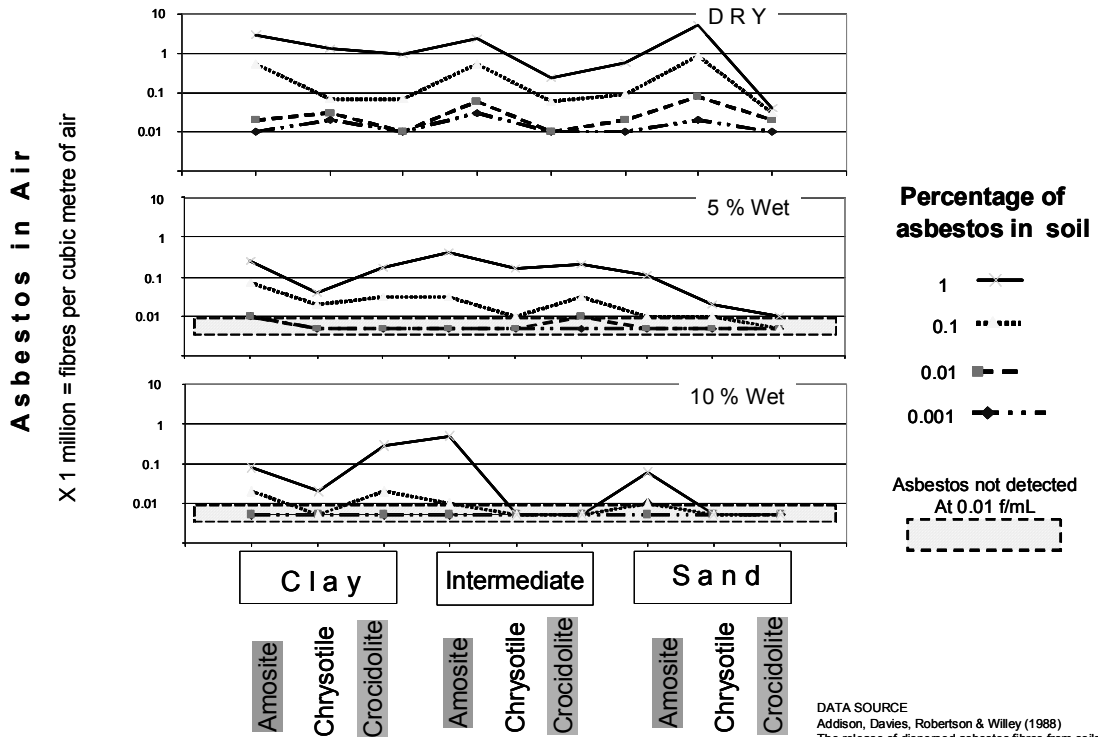


Fig. 1. Risk of death from lifetime exposures, based on the USEPA risk calculator.

Asbestos in air related to soil amount, mineralogy, soil type and soil moisture



MVA 2008

Fig. 2. Asbestos in soil related to various levels of Risk of death from lifetime exposures, based on the USEPA risk calculator.

LNAPL TRANSMISSIVITY – THE EMERGING METRIC FOR HYDRAULIC RECOVERY

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Risk-based management of dissolved-, vapor- and soil-phase contamination is based on sound science (e.g., ASTM, 1995) and has been adopted by many regulatory frameworks. However, the state of practice for managing free LNAPL (a.k.a. free product) is still generally not based on scientific principles. Many regulatory frameworks require that free LNAPL be recovered to the extent practicable. A small in-well LNAPL thickness is usually used as an indicator of practicability (e.g., 0.002 m), i.e., as a start and end point for hydraulic recovery of LNAPL. While in-well LNAPL thickness may be easy to measure, it is a poor indicator of recoverability. Often an endpoint based on in-well thickness is difficult to achieve via hydraulic recovery, which has led to hydraulic-recovery systems running perpetually with little improvement in environmental conditions.

In recent years, there have been significant advances in the understanding of LNAPL behavior, including recognition of limitations of hydraulic recovery and the development of alternative metrics for hydraulic recovery (ASTM, 2006; ITRC, 2009). One emerging metric of LNAPL recoverability is LNAPL transmissivity. LNAPL transmissivity is a lumped measurement of all parameters that affect LNAPL recoverability, viz., soil conductivity, LNAPL saturation, thickness of mobile LNAPL interval and LNAPL viscosity. It is a leading and lagging metric, i.e., it serves both as a start and endpoint.

This presentation will provide an overview of the advances made in recent years for managing LNAPL-impacted sites, with a focus toward alternative metrics of hydraulic recovery, especially LNAPL transmissivity. The presentation will also provide examples of use of emerging metrics such as LNAPL transmissivity for hydraulic recoverability at LNAPL-impacted sites.

REFERENCES

ASTM, (1995) *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, ASTM E1739

ASTM (2006) *Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface*, ASTM E2531

ITRC (2009) *Evaluating LNAPL Remedial Technologies for Achieving Project Goals. LNAPL-2*. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team.

MANAGEMENT OF SOIL AND GROUNDWATER CONTAMINATION IN THE CONTEXT OF SATISFYING CUTEF

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INTRODUCTION

Two (2) former industrial sites with long complex histories of heavy manufacturing were subjected to comprehensive environmental investigation, risk assessment and considered, targeted but limited remediation during environmental audits carried out at the properties. Submissions prepared for Victorian Environment Protection Authority (EPA) review support the position that Cleanup to the Extent Practicable (CUTEF) has occurred with respect to contaminated groundwater and its likely sources. The EPA has concurred that CUTEF had been achieved at both sites.

BACKGROUND

Melbourne, Victoria has long been associated with heavy industry, and brownfield properties in older sections of Melbourne are a common legacy of this history. The subject properties, located in North Melbourne and Richmond, were utilised for automotive parts manufacturing (chiefly springs and other suspension components) and a foundry, respectively, each for close to 100 years. The automotive parts manufacturing business incorporated a number of the neighbouring properties and site history review indicated initially a tannery also operated at the property. Similarly, the heavy industry foundry business was carried out on adjacent properties some of which were quarried during the 1930s and 1940s.

As brownfields, these sites were not providing beneficial use for the community. To enable their re-use without committing to cost-prohibitive complete remediation of contaminants required careful and thorough investigation, considered evaluation of applicable remedial technologies and detailed assessment of risks to human health and the environment.

ASSESSMENT

The multiple aquifers present at each site required depth discrete groundwater sampling under difficult drilling conditions. Hydrogeological characterisation included slug testing and collection of parameters to understand adsorption, leaching and migration potential. Both sites were located in close proximity to potential surface water receptors protected by State Environment Protection Policies (SEPPs).

The properties were subjected to removal of contaminants by excavation and offsite disposal. Accordingly, the remediation was limited with a significant amount of contaminated soils remaining at the sites. In the case of the North Melbourne site removal of contamination was targeted whilst in the case of the Richmond site, removal occurred as a result of basement excavation.

Alternatives for further remediation for the North Melbourne site were first screened using the United States Environmental Protection Agency (USEPA) Federal Remediation Technology Roundtable (FRTR) Remediation Technology Screening Matrix tool. Technologies indicated to be above average for the contaminants and conditions were evaluated further for cost,

logistics and technical considerations (feasibility). Given the Victorian EPA waste hierarchy requirements, technologies were also assessed against the principles of sustainability.

Detailed risk assessment for the North Melbourne site included evaluation of vapour risks, non-aqueous phase liquid (NAPL) mobility and recoverability and natural attenuation modelling for a number of organic contaminants including some chlorinated solvents. NAPL mobility and recoverability review was carried out using American Petroleum Institute (API) methods based on site-specific values for some parameters and conservative literature values for others. Based on the conservative review, the NAPL was determined to be immobile and not recoverable and no additional site-specific data was sought.

For the North Melbourne site, the level of risk to human health and the environment was determined to be low. Review of remedial options for environmental benefit, technical, logistical and financial considerations indicated containment by capping, as part of the proposed development, to be the preferred alternative.

Containment presented a highly feasible option that was viable alongside the proposed industrial use. Capping was considered to be low cost, sustainable given its low power, fuel and infrastructure consumption, effective at reducing the key risks posed and strongly aligned with the waste management hierarchy principles from the Environmental Protection Act (1970).

The Richmond site risk assessment focussed on examining the potential for remaining inorganic contaminants to migrate from soil and groundwater to the closest water receptor, the Yarra River. Although some information was available to calibrate fate and transport modelling, data had only been collected intermittently. Given the sensitivity of the modelling to adsorption coefficient values (K_d), available data was carefully examined to establish best estimates for this parameter, specifically synthetic precipitate leaching procedure (SPLP) results. Work by Townsend et al, 2008 was reviewed to understand whether SPLP data could be used to determine functional K_d values.

Conservative modelling together with knowledge of the spatial distribution of contaminated materials at the surrounding properties provided a good understanding of the conceptual site model on which to base decisions. The work was able to conclude that onsite and offsite receptors would not be subjected to unacceptable risks by site contaminants. As for the North Melbourne site, containment by capping as part of the proposed development was considered to be acceptable for the Richmond site.

CONCLUSIONS

The redevelopment of these sites has sought to maximise benefit for the cost while ensuring that reconstruction works are managed safely and the long-term risks to the environment are minimised. The CUTEP submissions for both the Richmond and North Melbourne sites were developed in a manner that successfully demonstrated that the sites were suitable for their development scenarios and beneficial uses, i.e. commercial/industrial, high density residential and open space. In particular, the submissions provided supporting arguments based on in-depth assessment on critical inputs including hydrogeological characterisation and model conceptualisation, together with technical, financial and logistical considerations of remedial alternatives.

Townsend, T, Dubey, B and Tolaymat, T, 2006, Interpretation of Synthetic Leaching Procedure (SPLP) Results For Assessing Risk to Groundwater from Land-Applied Granular Waste, Environmental Engineering Science, Volume 23, Number 1

THE PROBLEM OF CHANGING PRACTICES AND DECISION MAKING IN CONTAMINATED SITES MANAGEMENT

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INTRODUCTION

In broad terms, the contaminated site assessment and management process is intended to ensure that i) risks to human health and the environment are appropriately assessed, and ii) where unacceptable risks to human health and/or the environment are identified, these risks are appropriately managed. By necessity, contaminated sites consultants and regulators make contamination assessment related decisions based upon the understanding of chemical toxicities and best practice assessment methods which are in effect at the time. However, toxicity assumptions and best practice assessment methods are subject to regular change and there are currently no mechanisms in place to review the present day defensibility of assessments which have been made in the past. This raises the question of whether there is a flaw in the contaminated sites assessment and management system which is resulting in the inadequate protection of human health and the environment?

CHANGING BEST PRACTICE ASSESSMENT METHODS

Contaminated sites consultants and regulators rely on current best practice assessment methods when assessing the nature/extent of contamination and modelling potential exposures. The problem of changing best practice assessment methods refers to industry accepted best practice health/environmental risk assessment practices changing over time (e.g. analytical lists, sampling methodologies, modelling approaches etc).

The most obvious recent example of changing best practice assessment methods in Australia is the assessment of the vapour intrusion pathway (e.g. see proposed changes to the National Environment Protection Measure). It is considered likely that numerous contaminated sites across Australia have been 'signed off' by regulators without consideration of the vapour intrusion pathway or on the basis of indefensible vapour risk assessment methodologies. It is noted that although some historical soil gas modelling practices could be over-conservative, they were not implicitly over-conservative and the methods were also used to provide non-conservative estimates (e.g. Hers et al, 2003).

In addition to changing assessment methods relating to how chemical concentrations are measured and modelled, what chemicals are measured also changes. For example, petroleum hydrocarbon concerns were historically limited to BTEX (i.e. benzene, toluene, ethylbenzene, xylenes), however, more recent search also points to other concerns.

The following example relates to a current project in Victoria which illustrates the point well. The initial investigations were completed in the late 1990s and focused on soil contamination only (i.e. asbestos). A regulator accredited auditor 'signed off' on the project as being suitable for a proposed commercial/industrial development so long as contaminated fill materials were appropriately capped. In the early 2000s a new commercial/industrial development was proposed which triggered a second audit. By the time of the second audit, not assessing groundwater contamination had become less acceptable. Groundwater investigations identified a site originated petroleum hydrocarbon plume and an offsite originated chlorinated solvent plume. These groundwater investigations triggered soil gas investigations which identified that future commercial/industrial buildings required vapour mitigation measures. In the absence of a second proposed development and trigger for a second audit, the groundwater and soil gas contamination issues would have remained unidentified. It is suspected that there are many sites in Australia with similar issues.

CHANGING TOXICITY ASSUMPTIONS

Contaminated sites consultants and industry regulators rely on toxicity data when making assessments regarding the significance of risks posed by a chemical (i.e. basis for default criteria or site specific risk assessments). The problem of changing toxicity assumptions refers to the revision of previous toxicity assessments and the provision of new toxicity assessments.

A number of recognised bodies produce chemical toxicity assessments which are specific to exposure routes and individual or groups of chemicals. These assessments are infrequently reviewed and occasionally altered after initial publication. For example, the United States Environment Protection Agency (US EPA) is currently in the process of revising its position regarding the toxicity of tetrachloroethylene (US EPA, June 2008). As toxicity assessments are reviewed and revised, projects are not put on hold pending a final decision. Rather, the projects progress on the basis of the information which is available at the time.

For chemicals where no directly applicable and reliable toxicity assessments have been previously prepared, common practice is to i) extrapolate data for the same chemical/group from a different exposure route (e.g. oral to inhalation), ii) use toxicity data for a structural analogue, or iii) assume that the chemical is not significantly toxic. Obviously, contaminated site assessment projects are not put on hold until adequately reliable toxicity data is obtained for all chemicals of concern.

It is considered more than reasonable to assume that in the future the available toxicological information database will be improved and that this improvement may identify that some historical practices were inappropriate (e.g. ignoring chemical X, identifying new critical toxicological endpoint for chemical Y). Although the safety factors built into toxicity criteria provide some comfort, these safety factors do not discount the potential for some chemicals to be uniquely toxic to sub-populations or for principle studies to be found to be critically flawed. The safety factors obviously provide no comfort for chemicals where no reliable toxicity assessments are currently available.

CONCLUSIONS

Based on the identified problems, it is considered that the critical questions are: a) How many sites are there which have been 'signed off' by a regulatory authority on the basis of toxicological assumptions and/or assessment methods which are no longer acceptable? b) Of these sites, how many actually represent unacceptable risks to human health and/or the environment?, c) By what mechanism/s will regulators avoid similar situations in the future? Addressing Points a and b will require a significant amount of effort and cooperation between consultants, land owners and regulators. However, it is considered likely that there are a materially significant number of contaminated sites in Australia which have been signed off on the basis of outdated toxicity assumptions and/or assessment methods. It is considered that it is in the public interest to resolve this issue.

With regard to Point c, it is suggested that part of the solution is a contaminated sites cataloguing system. This system would require consultants and regulators to record key details for each contaminated site assessment in order to allow retrospective risk assessments in the future, as necessary.

REFERENCES

- United States Environmental Protection Agency (June 2008) Toxicological Review of Tetrachloroethylene (Perchloroethylene) (CAS No. 127-18-4), In Support of Summary Information on the Integrated Risk Information System (IRIS) (EPA/635/R-08/011A External Review Draft)
- Environment Protection and Heritage Council website, 'ASC NEPM Variation 2010 – Public Consultation Documents'. <http://www.ephc.gov.au/contam/pcdocs>.
- Hers, I., Zapf-Gilje, R. Johnson, P.C. and Li, L. (2003) Evaluation of the Johnson and Ettinger Model for Prediction of Indoor Air Quality. *Ground Water Monitoring & Remediation*, 23, 2, pp. 119-133.

OBSERVATIONS OF THE RANDOM APPROACHES TO REMEDATION PLANNING IN AUSTRALIA

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INTRODUCTION

In recent years, remediation of contaminated sites in Australia has increased in complexity due to land shortage, regulation, restrictions on use of the “dig and dump” approach for soil and an increased expectation of thorough groundwater remediation (e.g. CUTEF, RTEN). The latter is partly driven by water scarcity and increased recognition of groundwater as a vulnerable environmental element (GDEs etc). This, together with the greater availability and options for on-site and in-situ soil and groundwater remediation technologies, has made the use of alternative options more widespread. But this has also led to more complex remediation engineering design and implementation (not only for larger and complex sites but also for challenging issues like LNAPL, DNAPL and remediation of recalcitrant compounds), with higher degrees of uncertainty, possible failure, potential for ongoing liability and need for long term management.

Therefore, it would be expected that the regulatory agencies (i.e. state EPAs) would have provided increasing guidance on the remediation planning and implementation process. However, as previously discussed by the Authors (Lane & Gringinger, 2006) there is repetitious guidance on the site (and to some extent risk) assessment phases of the Contaminated Land Management (CLM) process and a dearth of guidance on the remediation planning components of the CLM process. Based on the Author’s experience, not much has changed since then, including the proposed revision of NEPM that provide no further guidance on remediation planning. Remediation planning in this context is viewed as the link between site and risk assessment and implementation of remedial measures. This should ideally include aspects like definition of remediation drivers, goals, objectives and targets, remediation options screening & evaluation, development of a remediation strategy followed by remedial investigations and feasibility studies, which should lead to a remedy selection, detailed design, specifications and implementation plans.

Taking a holistic point of view, to restore contaminated sites through the CLM life cycle to make them “fit for use”, it is the remediation stage which is the most expensive, time consuming and resource demanding, and is the most critical stage for the success or failure of a site revitalisation project. Some industry sources would say that the scale and cost of the majority of remediation projects in Australia are underestimated in the site assessment phase by up to 100%. The current shortage of remediation planning guidelines in Australia contrasts unfavourably with that available elsewhere (e.g. USA, Canada, UK and others – Gaboriau & Colombano, 2006, Lane & Gringinger, 2006). Significant potential for inadequate and under-costed or excessive and unnecessary remediation exists and has occurred frequently for poorly planned and implemented remediation programs. This is a waste of limited resources, which could be better directed elsewhere (where environmental improvement and sustainability can be achieved in real terms), as well as potentially causing ongoing or re-emerging management and legal liabilities.

It would be inconceivable to advance any serious engineering project of even moderate size directly from a preliminary scoping and evaluation stage into implementation, without prior feasibility assessment, detailed evaluation, detailed design, costing, and specifications (including peer review and sign off). However, this appears the approach still taken to a variable extent for many CLM projects in Australia.

METHODS

We have been involved in a number of remediation projects completed over recent years as part of the completion of statutory environmental Audits undertaken by the Authors or in our role as assessors and advisors. The review focused on the type and level of remediation planning approaches applied by the assessment consultants on these sites to determine (1) any use of remediation planning guidelines from other jurisdictions, (2) level of sophistication of remediation planning approach, and (3) success rate – i.e. adequacy of the remediation approach to achieve the desired project outcomes in the most cost-efficient manner. The review included many types of projects, of various sizes (both for sites and remediation costs), complexity (simple soil removal to complex large scale soil remediation), multiple groundwater plumes (including LNAPL & DNAPL), various settings (from sand to fractured rock) and a wide range of assessment consultants and client companies.

RESULTS AND DISCUSSION

The summary results of our review revealed the following results in relation to the questions posed:

- (a) There are no consistent commonalities (i.e. it appears to be random) of remediation planning approaches. These approaches appear to be highly individualised according to the methods adopted by particular companies (and often depending on the choice of personnel responsible for individual projects), such that there is a great variability in approach and risk management.
- (b) Occasional loose reference appears to be made to remediation planning approaches (and terminology) from other jurisdictions, most prominently from the UK, which may also reflect personal experience and background of remediation engineers involved in these projects.
- (c) The sophistication of remediation planning approaches generally increases with the size and complexity of the remediation project, but frequently still follows what has been previously described as the “conventional view” of the remediation process (Lane & Gringinger, 2006) including the widespread use of a RAP. However, the content and sophistication of RAPs are highly inconsistent (even though some guidance on RAPs exists in NSW and WA), including the random use of terminology/jargon. In many of these, remediation planning approaches were incomplete or superficial, without predefined planning logic, or without the use of a CLM life cycle approach and an outcome focussed (end-in-mind) approach, in contrast to those in other jurisdictions.
- (d) Because most reviewed remediation projects were undergoing statutory Audits (some are still in progress) it is conceivable that the desired project outcomes were or could be achieved (i.e. Audit completion), however significant delays (in Audit and/ or project completion process), re-work, additional reviews, additional work, and at times onerous management requirements as well as significant cost overruns occurred on many projects. In our opinion this reflects the inadequacy of the remediation planning process for these projects.

CONCLUSIONS

Our review presented in this study and previous work (Lane & Gringinger, 2006) confirms that the lack of Australian guidelines for the remediation planning process is not only unsatisfactory and at times frustrating for all stakeholders but places an excessive burden (financial, resources, time and liability) on site redevelopers. This is likely to continue and may worsen with the prevailing trend of increasingly sophisticated on-site and in-situ remediation approaches. Hence, to provide for better, more effective and efficient remediation success, planning guidelines are an essential tool in the CLM life-cycle tool box. This study shows the need for national guidelines for a sensibly structured but flexible remediation planning process and its details. If regulators are not willing to develop these guidelines, then professional organisations (e.g. ACLCA, ALGA) in cooperation with other stakeholders (e.g. EPAs, CRC CARE etc) should lead the way.

USE OF IN VITRO OR SOIL PROPERTY MODELS TO ASSESS TOXIC METAL BIOAVAILABILITY IN SOIL: VALIDATION TO SUPPORT REGULATORY ACCEPTANCE

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INTRODUCTION

The U.S. Department of Defense (DoD) along with other U.S. Federal facilities face a potentially daunting task of remediating thousands of metal contaminated sites within the U.S. and its territories, which contain unacceptable levels of toxic metals. With the exception of Pb contaminated soils, human health and ecological risk drivers have prompted U.S. Environmental Protection Agency to assume that the total soil metal concentration is 100% bioavailable. Previous SERDP funded research (ER-1166, ER-1210), however, has shown that metal-sequestering properties of soil can significantly lower the bioavailability and risk of heavy metals to human and ecological receptors (e.g. plants, soil invertebrates). Key soil properties controlled the toxic metal bioaccessibility measured using in vitro methods that simulated the digestive system of humans (Whitacre, 2009; Yang et al., 2002). Based on these findings, measurement of key soil properties could be used as an indicator tool at DoD sites to determine whether site remediation is necessary or whether more definitive site-specific in vivo metal bioavailability studies are warranted. Nevertheless, site-specific use of the predictive tool is impeded by the lack of regulatory acceptance. This is rational due to the lack of site-specific investigations that couple in vivo bioavailability and in vitro bioaccessibility studies with soil properties. The objective of this study was to evaluate the ability of previously researched in vitro and soil property models to predict metal(loid) human and plant bioavailability in soils from various locations.

METHODS

Soils were collected from twelve U.S. DoD or U.S. Department of Energy locations. Key soil properties, total metal(loid) content, bioaccessibility and bioavailability were determined. Human bioavailability via soil ingestion exposure pathway was assessed by in vitro gastrointestinal bioaccessibility methods including the Relative Bioavailability Leaching Procedure (RBALP)(Drexler and Brattin, 2007) for Pb. The Ohio State University In Vitro Gastrointestinal Method (OSU IVG)(Basta et al. 2007) and the SBET method (Juhasz et al. 2009) were used to assess oral bioavailability of As. Relative bioavailability (RBA) or relative bioaccessibility (IVBA) was calculated from previously published predictive equations using measured bioaccessibility (Basta et al., 2007; Drexler and Brattin, 2007; Juhasz et al. 2009) and (2) soil properties (Whitacre, 2009; Yang et al. 2002). Predicted RBA were compared with measured RBA using the juvenile swine model for select soils. For ecological risk estimates, metal phytoavailability was determined lettuce (*Lactuca sativa L. var. longifolia*) and perennial ryegrass (*Lolium perenne*) bioassays. Phytoavailability was estimated from soil-property driven multiple regression models developed using bioaccumulation data from a previous study (Dayton et al., 2006). A separate approach involved the use of soil extraction methods to predict metal(loid) bioavailability. Comparison of the actual metal(loid) phytoaccumulation from bioassays with predicted phytoaccumulation from soil extraction or soil property-driven models were used to quantify

the ability of these models to predict actual phytoaccumulation in field soils. This was the basis for validation of the soil property or soil extraction methods for field soils.

RESULTS AND DISCUSSION

In vivo RBA Pb for a selected study soil was 83.3% with a 90% confidence interval (CI) ranging from 70% to 127%. Relative Bioavailable Pb of 83.3% determined by RBALP showed this method was an accurate predictor of in vivo RBA Pb. In vivo RBA As for a select study soil was 14% with a 90% CI ranging from 13% to 15%. Relative Bioavailable As of 15.0 determined by OSU IVG and 12.2% by SBET RBALP showed both methods were an accurate predictor of in vivo RBA As. Good prediction of As bioaccessibility was achieved using soil property models of Whitacre (2009) and of Yang et al. (2002) for most soils. However, results for all soil showed the ability of soil properties to predict bioaccessible As is source dependent. With few exceptions, both soil property and soil extraction models were able to predict phytoavailability. In general, soil property models were predictive of tissue As, Cd, and Pb. Similar findings were found for soil extraction models. However, soil extraction models over predicted ryegrass tissue As for all soils.

CONCLUSIONS

Use of in vitro methods to predict human RBA Pb and As is very promising. Limited results from this study show the in vitro methods can be highly predictive. Predictive models using select soil properties can also be highly predictive of bioaccessible As. It is very possible that the poor prediction of soil properties to predict bioaccessible As in one of the soils may be due to different arsenic speciation in this contaminated soil. Further research on the effect of contaminant speciation of different contaminant sources on the ability of various in vitro methods to predict RBA As is needed and is underway. Both soil property and soil extraction models were predictive of tissue lettuce Pb, Cd, and As and of tissue ryegrass Pb and Cd. However, there were exceptions for several soil-contaminant combinations. Further validation studies of these methods for other contaminated soils from different contaminant sources are warranted.

REFERENCES

- Basta, N.T., Foster, J.N. Dayton, E.A., Rodriguez, R.R., Casteel, S.W. (2007) The effect of dosing vehicle on arsenic bioaccessibility in smelter-contaminated soils. *J. Environ. Health Sci. Part A*. 42:1275-1281.
- Dayton, E.A, Basta, N.T., Payton, M.E., Bradham, K.D., Schroder, J.L., Lanno, R.P. (2006) Evaluating the contribution of soil properties to modifying lead phytoavailability and phytotoxicity. *Environ. Toxicol. Chem.* 25:719-725.
- Drexler, J.W., Brattin, W.J. (2007) An *in vitro* procedure for estimation of lead relative bioavailability: With validation. *Human Ecol. Risk Assess.* 13:383-401.
- Juhasz A.L., Weber J., Smith E., Naidu R., Rees M., Rofe A., Kuchel T., Samson, L. (2009) Assessment of four commonly employed in vitro arsenic bioaccessibility assays for predicting in vivo relative arsenic bioavailability in contaminated soils. *Environ Sci. Technol.* 2009; 43: 9487-9494.
- Juhasz, A.L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Samsom, L., Naidu, R. (2007) In vitro assessment of arsenic bioaccessibility in contaminated (anthropogenic and geogenic) soils. *Chemosphere* 69:69-78.
- Whitacre, S. D. (2009) Soil controls on arsenic bioaccessibility: Arsenic fractions and soil properties. M.S. Thesis. The Ohio State University, Columbus, OH USA.
- Yang, J.K., Barnett, M.O., Jardine, P.M., Basta, N.T., Casteel, S.W. (2002) Adsorption, sequestration, and bioaccessibility of As (V) in soils. *Environ. Sci. Technol.* 36:4562-4569.

BIOAVAILABILITY/BIOACCESSIBILITY OF ORGANIC CONTAMINANTS IN SOIL: FUNDAMENTALS TO APPLICATION

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The fate and behaviour of organic contaminants in soils has been subject of intensive research, with particular interest directed at the bioavailability of contaminants. Interactions between contaminants and biota in soil are complex, controlled by physico-chemical properties of soils and contaminants, type of organism and its activity, as well as time. The term 'bioavailability' has generated considerable debate in the literature and, as a result, there has been considerable confusion over what is actually meant by 'bioavailability'. Recently, Semple et al. (2004) defined bioavailability and bioaccessibility in a clear and unambiguous manner. Bioavailability was defined as the contaminant fraction 'which is freely available to cross an organism's (cellular) membrane from the medium the organism inhabits at a given point in time.' Whereas, bioaccessibility encompasses what is actually bioavailable now plus what is 'potentially bioavailable' Assessment of the bioavailability and bioaccessibility of organic contaminants in soils is essential to understanding the risk posed by the contaminant and the means required for successful remediation.

Over the last two decades there have been considerable efforts to develop chemical techniques which describe bioavailability of organic contaminants in soil. A number of chemical extractants have been proposed to determine the fate and putative bioavailability of HOCs in freshly spiked and aged soils. Ultimately, chemical techniques have been developed to gain knowledge about the bioavailability contaminants in soils, within shorter time periods and lower budgets; biological techniques or bioassays may be time consuming and laborious. Traditionally, analytical soil extraction techniques have been concerned with the determination of total chemical concentrations by exhaustive methods using organic solvents. Exhaustive techniques often provide an inappropriate means of assessing contaminated land for risk and remediation. It is suggested that regulations based on vigorous extractions, to establish goals for remediation and for the analyses of potential future releases or dissipation of organic contaminants in soil, do not appropriately estimate exposure or risk to susceptible populations. Subsequently, an extraction procedure that mimics or parallels bioavailability/bioaccessibility is preferable for assessing exposure and bioremediation potential. Such procedures are often referred to as biomimetic techniques. Recently, many studies have shown that harsh solvent extractions do not provide a realistic determination of the bioavailable fraction of organic contaminants in soil. Sufficient evidence has been gathered to show that the vigorous or harsh extraction techniques currently used to estimate the concentration of organic pollutants in soil overestimate often appreciably the levels that are actually bioavailable or bioaccessible.

Considerable effort has been directed towards developing non-exhaustive chemical techniques for the measurement of putative contaminant bioavailability. Non-exhaustive techniques are mostly based on the principle that bioavailability, in particular to microorganisms is governed by contaminant mass transfer mechanisms such as desorption from solid to aqueous soil phases (Bosma et al., 1997). Many authors have proposed the use of mild extractants for a more viable and accurate assessment or prediction of bioavailable contaminant fractions. However, the complexity of interactions between the physico-chemical properties of the contaminant, the soil and the biota in question, make solvent extractions unreliable predictors of bioavailable fractions. Several disadvantages or limitations of utilising mild solvent extraction have been outlined, such as (i) the type of solvent used (i.e. polar or non-polar solvent, e.g. methanol or hexane, respectively), ii) the nature of the extraction (e.g.

soxhlet, shake, supercritical fluid) and iii) the impact of the extraction procedure on the physico-chemical properties of the soil. Subsequently, a range of non-exhaustive extraction techniques that are not dependent on organic solvents have been considered for bioavailability prediction such as solid phase extraction (Tenax beads and XAD resin), supercritical fluid extraction, C18 membranes, persulphate oxidation and cyclodextrin extraction. These have been reviewed by Semple et al. (2007).

The group at Lancaster University has pioneered the application of cyclodextrin extractions of organic contaminants in soils and sediments (Reid et al., 2000). Numerous studies have shown investigated the use of cyclodextrin extraction as a predictor for microbial degradation of PAHs in single contaminant-spiked soils, multiple PAH spiked soils and field contaminated soils. In each case, the cyclodextrin extraction directly predicted the extent to which the PAHs would be degraded. This has been confirmed by other groups, for example, Cuypers et al (2001) where two sediment samples were sequentially extracted with aqueous solution of HPCD and Triton-X; PAH removal during extraction was then compared with PAH removal during biodegradation and solid phase extraction (Tenax). It was demonstrated that HPCD extraction followed Tenax and removed primarily readily available PAHs.

Overall, many studies reporting on the availability/accessibility of chemicals in soil have focused on the relationship between contaminant extractability (to organic solvents or hydrophobic resins) and microbial degradation using a catabolically active inoculum. As a result, two things are measured: (i) measurement of bioaccessibility rather than bioavailability and (ii) a measure of degradation relying on inoculation of allochthonous organisms - perhaps mimicking inoculant-dependant bioremediation strategies. Further, the measurement of bioaccessible concentration prior to bioremediation and hence a determination of the likelihood of reaching particular concentrations deemed 'safe' would be an extremely useful tool in the assessment of contaminated land and in making informed decisions about the suitability of a biological technique for the remediation of contaminated land.

USE OF IN VITRO TECHNIQUES TO PREDICT THE RELATIVE BIOAVAILABILITY OF ARSENIC, CADMIUM AND LEAD VIA THE INCIDENTAL SOIL INGESTION PATHWAY

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INTRODUCTION

Incidental ingestion of contaminated soil is a major non-dietary exposure pathway for many inorganic contaminants. In order to more accurately quantify exposure to inorganic contaminants via soil ingestion, determination of contaminant bioavailability is required. In vivo assays using a variety of animal models (e.g. primate, swine, dog, rabbit, rodent) have been used to quantify the relative bioavailability of contaminants in soil (Juhasz et al., 2007). However, given the time and cost requirements, in addition to ethical issues, there is great demand for an appropriate in vitro assay for estimating contaminant relative bioavailability. In vitro assays are simple, rapid and inexpensive and numerous methods have been applied for the determination of contaminant bioaccessibility (Juhasz et al., 2009). However, before these assays can act as a surrogate measure for relative bioavailability, correlation between in vitro bioaccessibility and in vivo relative bioavailability is a mandatory prerequisite for regulatory as well as scientific acceptance. This paper discusses the development and assessment of in vitro assays for predicting the in vivo relative bioavailability of soil contaminated with arsenic (As), cadmium (Cd) and lead (Pb).

METHODS

Arsenic, Cd and Pb contaminated soils were sourced from urban and regional areas in Australia where the soil type, source and contaminant-soil residence time varied. Soils were air dried then sieved and the <250 µm particle size fraction retained for chemical characterisation and bioaccessibility / relative bioavailability assessment. Contaminant bioaccessibility was determined using SBRC, IVG, PBET and DIN assays incorporating both gastric and intestinal phases (Juhasz et al., 2009). At the completion of gastric or intestinal phase extraction, samples were filtered (0.45 µm) prior to analysis by ICP-MS. In vivo relative bioavailability studies were approved and conducted according to the IMVS Animal Ethic Committee and the Guidelines for the care and use of laboratory animals. Arsenic and Pb relative bioavailability was determined using a swine model according to Rees et al., (2009) encompassing area under the blood-concentration time curve analysis. The concentration of As and Pb in blood was determined by ICP-MS according to Agilent Technologies (2006). In vivo Cd bioavailability studies were conducted with mice by incorporating Cd acetate (reference dose) or Cd contaminated soil into formulated mice pellets. Individual mice were fed 2 g of the respective feed mix once daily over a 15 day exposure period. At the end of the exposure period, the concentration of Cd in the kidneys and liver was determined by ICP-MS following tissue digestion. Arsenic, Cd and Pb relative bioavailability, derived from in vivo mouse or swine assays, was compared to bioaccessibility data determined using SBRC, IVG, PBET and DIN methods. Bioaccessibility-relative

bioavailability best fit models were determined using stepwise multiple regression (SPSS 16.0.1).

RESULTS AND DISCUSSION

For all four in vitro methods, As, Cd and Pb bioaccessibility was greater when gastric phase values were compared to the intestinal phase. Due to the low pH environment of the gastric phase, release of As, Cd and Pb from the soil matrix occurred as a result of dissolution processes which are dependent on mineralogy in addition to the gastric phase pH of the in vitro method. Generally the gastric phase of the SBRC assay produced the highest bioaccessibility results presumably due to the differences in pH values of the four in vitro methodologies (1.5 versus 1.8, 2.0 and 2.5). Increasing the pH from gastric to intestinal phase conditions resulted in a significant decrease in As, Cd and Pb bioaccessibility presumably due to co-precipitation with and/or sorption to iron. Relative bioavailability varied significantly between contaminated soils ranging from $6.9 \pm 5.0\%$ to $74.7 \pm 11.2\%$ for As, $10.1 \pm 0.4\%$ to $92.1 \pm 7.3\%$ for Cd and $10.1 \pm 8.7\%$ to $19.1 \pm 14.9\%$ for Pb. When linear regression models were developed in order to determine the suitability of in vitro assays for predicting As, Cd and Pb relative bioavailability, the correlation between bioaccessibility and relative bioavailability varied depending on the methodology used. While As, Cd and Pb relative bioavailability could be accurately predicted using SBRC-G, PBET-I and Rel-SBRC-I respectively (Table 1), a single in vitro method was not suitable for predicting relative bioavailability for all three contaminants.

Table 1. Best fit linear regression models for predicting in vivo As, Cd and Pb relative bioavailability using in vitro assays.

Contaminant	In vitro assay/phase	In vivo-in vitro predictive model	Pearson correlation
As (n=12)	SBRC-G	$RBA (\%) = 0.992 * SBRC-G (\%) + 1.656$ $R^2 = 0.754$	0.868
Cd (n=7)	PBET-I	$RBA (\%) = 1.091 * PBET-I (\%) - 5.140$ $R^2 = 0.835$	0.914
Pb (n=5)	Rel-SBRC-I ^a	$RBA (\%) = 0.580 * Rel-SBRC-I (\%) + 1.980$ $R^2 = 0.530$	0.730

^aPb Relative bioaccessibility in the intestinal phase of the SBRC assay was calculated by adjusting the dissolution of Pb from contaminated soil by the solubility of Pb acetate at the corresponding pH value (pH 6.5).

CONCLUSIONS

When in vivo As, Cd and Pb relative bioavailability data was compared to bioaccessibility data, simple, rapid, inexpensive in vitro assays could accurately predict relative bioavailability.

REFERENCES

- Agilent Technologies. 2006. Determination of heavy metals in whole blood by ICP-MS. Agilent Technologies publication number 5988-0533EN.
- Juhasz, A.L., Smith, E., Weber, J., Naidu, R., Rees, M., Rofe, A., Kuchel, T., Sansom, L. (2009). Assessment of four commonly employed in vitro arsenic bioaccessibility assays for predicting in vivo relative arsenic bioavailability in contaminated soils. *Environ. Sci. Technol.* 43: 9487-9494.
- Juhasz, A.L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., Naidu, R. (2007). Comparison of in vivo and in vitro methodologies for the assessment of arsenic bioavailability in contaminated soils. *Chemosphere* 69: 961-966.
- Rees, M., Sansom, L., Rofe, A., Juhasz, A.L., Smith, E., Weber, J., Naidu, R., Kuchel, T. (2009). Principles and application of an in vivo swine assay for the determination of arsenic bioavailability in contaminated matrices. *Environ. Geochem. Health* 31: 167-177.

DESIGNING STRATEGIES TO INCREASE BIOAVAILABILITY IN BIOREMEDIATION OF PAHs

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INTRODUCTION

A major factor limiting the success of bioremediation of polycyclic aromatic hydrocarbons (PAHs) in polluted sites is the low bioavailability of these compounds, due to the slow release from the contaminated matrix. The resulting residual concentrations are of strategic value because they can limit future uses of the sites after treatment. Therefore, innovative methods are needed to increase bioavailability of these pollutants for an enhanced bioremediation performance. The present contribution will summarize our recent research efforts in this issue, performed in the Biodegradation and Bioremediation group at IRNAS-CSIC, Spain.

BIOAVAILABILITY-PROMOTING STRATEGIES

Surfactant application to promote biodegradation of slow-desorption PAHs

We employed a soil originated from a creosote-polluted site, and a manufactured gas plant soil that had been treated by bioremediation (Bueno-Montes et al., 2011). The two soils differed in their total content in five indicator 3-, 4- and 5- ring PAHs (2923 mg kg⁻¹ and 183 mg kg⁻¹ in the creosote-polluted and bioremediated soils, respectively) but had a similar content (140 mg kg⁻¹ vs. 156 mg kg⁻¹) of slowly desorbing PAHs. The PAHs present in the bioremediated soil were highly recalcitrant. The surfactant at a concentration above its critical micelle concentration enhanced the biodegradation of slowly desorbing PAHs in suspensions of both soils, but it was especially efficient with bioremediated soil. An inhibition of biodegradation was observed with the high-molecular-weight PAHs pyrene and benzo[a]pyrene in the untreated soil, possibly due to competition effects with other solubilized PAHs present at relatively high concentrations. We suggest that nonionic surfactants may improve bioremediation performance with soils that have previously undergone extensive bioremediation to enrich for a slowly desorbing profile.

Integrating electrokinetics and bioremediation

The use of electroosmotic flow for the treatment of hydrophobic organic soil-contaminants has recently been addressed as a relevant innovative step in soil remediation. However, to our knowledge, there have been limited attempts (documented) to connect these two technologies with remediation of PAHs. Our results indicate that biodegradation and electroosmosis can be successfully integrated to promote the removal of PAHs (Niqui-Arroyo & Ortega-Calvo, 2010). An electrokinetic pre-treatment was evaluated as a way to mobilise the less bioaccessible fraction of PAHs. Residual concentrations of total biodegradable PAHs, remaining after bioremediation in soil slurries, were twofold lower in electrokinetically pre-treated soils than in untreated soils. It is conceivable that physicochemical changes produced in polluted soil particles that were exposed to electric fields may promote bioaccessibility, thus improving bioremediation performance.

Interface fertilization of free-oil phases (NAPLs)

We used an oleophilic biostimulant (S-200) to target possible nutritional limitations for biodegradation of PAHs at the interface between NAPLs and the water phase (Tejada-

Agredano et al., 2011). Biodegradation of PAHs present in fuel-containing NAPLs was slow and followed zero order kinetics, indicating bioavailability restrictions. The biostimulant enhanced the biodegradation, producing logistic (S-shaped) kinetics and ten-fold increases in the rate of mineralization. The enhancement was not the result of an increase in the rate of partitioning of PAHs into the aqueous phase. It was neither caused by the compensation of any nutritional deficiency in the medium. Biodegradation of PAH by bacteria attached to NAPLs can be limited by nutrient availability due to the simultaneous consumption of NAPL components, but this limitation can be overcome by interface fertilization.

Modulating deposition and motility of degraders in porous media

The positive effects of mobilization approaches in bioremediation depend on the efficiency of bacterial movement in porous media, which is often restricted by high deposition rates and adhesion to soil surfaces. We have prospected bacterial taxis as a process which may help to overcome this limitation (Velasco-Casal et al., 2008; Ortega-Calvo et al., 2011; Jimenez-Sanchez et al., in prep.). In well-controlled column systems, we assessed the influence of different chemoeffectors on deposition of chemotactic, naphthalene-degrading bacteria in selected porous environments (sand, forest soil, and clay aggregates). Deposition, however, depended on the tactic response (attraction or repellence), its interaction with the column packing material, and concomitantly its pore-water concentration.

Promoting bioavailability with plants

The present contribution will summarize the overall design and most recent results of a Spanish national project (CGL2010-22068-C02-01) focused on PAH bioremediation and bioavailability in the rhizosphere. The ongoing project has already demonstrated the potential of plants from *Helianthus annuus* to promote bioavailability, and therefore biodegradation, of PAHs in soil (Tejeda-Agredano et al., in prep.). The experiments included 1) bioremediation assays in green-house microcosms with creosote-polluted soils, 2) in vitro-production of root exudates and 3) capillary and column chemotaxis assays with exudates and rhizosphere bacteria.

REFERENCES

- Bueno-Montes, M., Springael, D., and Ortega-Calvo, J. J. (2011) Effect of a non-ionic surfactant on biodegradation of slowly desorbing PAHs in contaminated soils. *Environ. Sci. Technol.* 45:3019-3026.
- Jiménez-Sánchez, C. and Ortega-Calvo, J. J. Role of tactic response on bacterial deposition during transport in porous media. *Environ. Sci. Technol.* (in preparation).
- Niqui-Arroyo, J. L. and Ortega-Calvo, J. J. (2010) Effect of electrokinetics on the bioaccessibility of polycyclic aromatic hydrocarbons in polluted soils. *J. Environ. Qual.* 39:1993-1998.
- Ortega-Calvo, J. J., Molina, R., Jimenez-Sanchez, C., Dobson, P. J., and Thompson, I. P. (2011) Bacterial tactic response to silver nanoparticles. *Environ. Microbiol. Rep.* (in press - doi:10.1111/j.1758-2229.2011.00252.x).
- Tejeda-Agredano, M. C., Gallego, S., Vila, J., Grifoll, M., Ortega-Calvo, J. J., and Cantos, M. Influence of sunflower rhizosphere on the bioaccessibility and biodegradation of PAHs in polluted soil. *Soil Biol. Biochem.* (in preparation).
- Tejeda-Agredano, M. C., Gallego, S., Niqui-Arroyo, J. L., Vila, J., Grifoll, M., and Ortega-Calvo, J. J. (2011) Effect of interface fertilization on biodegradation of polycyclic aromatic hydrocarbons present in nonaqueous-phase liquids. *Environ. Sci. Technol.* 45:1074-1081.
- Velasco-Casal, P., Wick, L.Y., and Ortega-Calvo, J.J. (2008). Chemoeffectors decrease the deposition of chemotactic bacteria during transport in porous media. *Environ. Sci. Technol.* 42:1131-1137.

ENHANCED DEGRADATION OF PYRENE BY AN ENVIRONMENTAL ISOLATE OF BACILLUS MEGATERIUM IN THE PRESENCE OF DIESEL

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INTRODUCTION

Bioaugmentation has been used as a strategy for the bioremediation of recalcitrant compounds in soil. For an organism to be a suitable candidate for this strategy it must meet several criteria: 1) it will survive and multiply once introduced to the system, 2) it will retain its degradative capacity within the system 3) it can be easily cultured and delivered to the system.

The purpose of this study was to investigate the pyrene degrading capability of a *B. megaterium* strain isolated from a former gas works site when reintroduced into contaminated soil. The strain was originally isolated from pyrene enrichment cultures supplemented with diesel, and subsequently the ability to degrade pyrene as sole carbon source in broth cultures was demonstrated (Gaskin and Bentham 2005). The ability of this organism to enhance degradation of pyrene when introduced into contaminated soil environments was the next stage in determining its potential for bioaugmentation. To monitor the activity of the *B. megaterium* in the soil microcosms two techniques were used. Firstly the removal of the pollutants (pyrene and diesel) was monitored using Gas chromatography. Secondly dehydrogenase activity as a surrogate for respiration was used to measure microbial activity in the soil systems.

METHODS

Bacterial inoculum grown in nutrient broth (*B. megaterium*) was added to triplicate 500g soil microcosms to give a bacterial concentration of approximately 10^3 organisms per g. The water holding capacity of the soil was also calculated and soil moisture was maintained at 50% water holding capacity via the addition of sterile water at each sampling day. Microcosms contained i) 200mg/Kg pyrene, ii) 200mg/Kg pyrene + 2000 mg/kg diesel. Control microcosms were also prepared with no bacterial inoculum added. Samples (30g) were sacrificed from each microcosm periodically for determination of pyrene concentration, and dehydrogenase enzyme activity. Dichloromethane extracts with internal standard of the soil were analysed for pyrene and diesel concentrations using a Varian 3800 gas chromatograph, equipped with a flame ionisation detector and using an Alltech EC-5 capillary column. Pyrene and diesel were used as the sole hydrocarbon sources. Dehydrogenase activity was assessed using the triphenyl tetrazolium chloride reduction method of van der Waarde *et al* (1995) using 1g of soil diluted in 9mL of phosphate buffered saline.

RESULTS AND DISCUSSION

Pyrene loss in soil microcosms containing *B. megaterium* was 121.496mg/Kg which equates to an observed pyrene loss of 57.4%. The majority of this loss occurred between days 3 and 21. A loss of 162.2mg/Kg (± 5.6) of diesel was also observed in these soil microcosms. This corresponds to an observed diesel loss of 76% with the majority of degradation occurring between days 0 and 21. An initial lag phase in pyrene degradation of 3 days was observed in soil microcosms containing *B. megaterium* (Fig. 1).

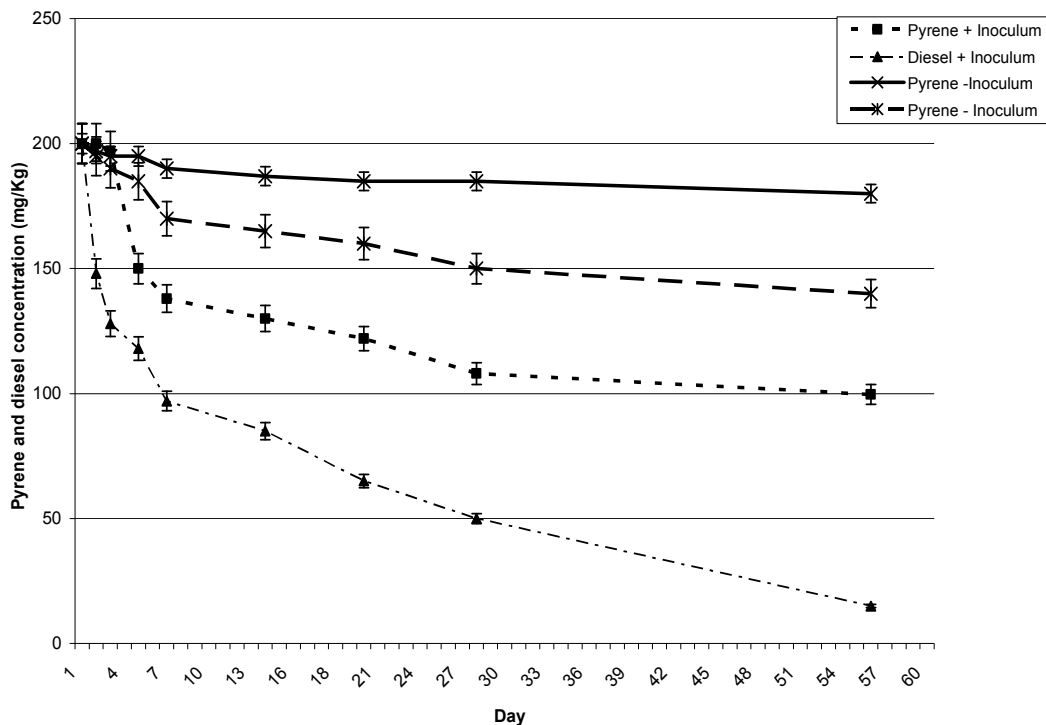


Figure 1. Pyrene and diesel concentrations in soil microcosms with and without *B.megaterium* inoculation.

Pyrene loss in unamended control soil microcosms was minimal (<5%). A diesel loss of 48.3 mg/Kg (± 3.3) was observed in these microcosms. This corresponded to a 24% loss of diesel in these systems. Statistical analysis demonstrated that amendment with the *B.megaterium* isolate significantly enhanced removal of both pyrene and diesel from the soil systems ($p=0.0001$, Fig. 2). Dehydrogenase activity in amended soil microcosms was significantly higher ($A_{max} 0.86$) than that observed in the control system ($A_{max} 0.46$) after an initial lag period in the first week ($p=0.005$), when activities were similar.

CONCLUSIONS

This study has demonstrated that bioaugmentation of a mixed aliphatic and aromatic hydrocarbon contaminated soil can be significantly enhanced by addition of a *B.megaterium* isolate. The isolate demonstrated its ability to survive and retain degradative capacity upon reintroduction. As a readily culturable spore-forming bacterium, it is a strong candidate for bioaugmentation of hydrocarbon contaminated sites.

REFERENCES

- Gaskin, S., and Bentham R. H. (2005) Comparison of enrichment methods for the isolation of pyrene-degrading bacteria. *International Biodeterioration and Biodegradation* 56: 80-85.
- Van der Waarde, J.J., Dijkhuis, E.J., Henssen, M.J., Keunig, S. (1995) Enzyme assays as indicators for biodegradation. In: Hinchee, R.E., Douglas, G.S. and Ong, S.K. (eds.) *Monitoring and verification of bioremediation*. Batelle press, Columbus – Richland. P59-63

MONITORING *IN SITU* BIOREMEDIATION OF HYDROCARBON-CONTAMINATED SOIL AT SUB-ANTARCTIC MACQUARIE ISLAND USING MICROBIAL ASSAYS AND FTIR

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INTRODUCTION

Macquarie Island, now a World Heritage Reserve, is part of Tasmania's territory almost 1500 kilometres southeast at 54°S. 159°E., isolated between Australia, New Zealand, and the Antarctic continent. It is a narrow plateau 34 km long and 5.5 km wide, with slopes up to 433 meters above sea level. Air temperatures vary only 4 – 4.5°C from mid winter to mid summer despite considerable variation in daylight hours. It receives about 1050 mm of precipitation per annum which falls on more than 320 days of the year. The majority of soils are known as Highmoor Peats and support tussock grassland and some herbfields. *Poa foliosa* Hook.f. (tussock grass) is the most abundant subantarctic grass and is widespread on Macquarie Island. The species has a long growing season and high productivity due to efficient use of low light levels and uniform temperature regime.

A previous joint study between the Australian Federal Government (Australian Antarctic Division (AAD)) and the Tasmanian State Government (Division of Environmental Management) assessed historically contaminated sites on Macquarie Island (Deprez *et al* 1995). This assessment found areas to be contaminated with petroleum hydrocarbons, including Special Antarctic Blend (SAB) diesel fuel. Soil total petroleum hydrocarbon (TPH) (C₉-C₂₈) concentrations in the affected areas are typically greater than 5 000 mg kg⁻¹ soil but as high as 19 000 mg kg⁻¹ soil. Vertically, the depth of hydrocarbon in the soil range from just below surface to 1.5 m below ground surface. Growth of *P. foliosa* is evident in both affected and adjacent unaffected areas.

There is a paucity of information available regarding the bioremediation of hydrocarbon contaminants in cold climates. Recent work in the Antarctic has shown the potential of microbial degradation of hydrocarbons at rates amenable to bioremediation (Ferguson *et al* 2008). Plant-assisted bioremediation (aka *rhizoremediation*) involves the *in situ* use of tolerant plant species and their associated micro-organisms to detoxify pollutants for the treatment of contaminated soils. The rhizosphere or root zone of plants is characterised by intense microbial activity. The exploitation of that increased microbial activity can assist in enhancing biotreatment of affected soil. Rhizoremediation of hydrocarbons using native Australian grass species has only recently been explored (Gaskin *et al* 2008; Gaskin & Bentham 2010), and focussed on warm and cool climates.

The investigation of rhizoremediation using biodiversity native to Macquarie Island is a unique and environmentally sustainable application of an important field of research.

Project objective: Evaluate the role of native sub-Antarctic Macquarie Island plants (*P. foliosa*; Tussock grass) in enhanced hydrocarbon remediation at Macquarie Island Station.

METHODS

A full scale *in situ* bioremediation project involving sub-surface aeration and nutrient addition of hydrocarbon-contaminated soil at sub-Antarctic Macquarie Island was initiated in summer 2009. The remediation program is anticipated to run for five years, and data presented here represents initial observations during the first summer season. During the remediation process monitoring of soil gas flux and microbial activity in areas with and without tussock grass was conducted over a four month period.

The flux of four gasses (CO₂, N₂O, CH₄ and NH₃) was measured using a Fourier Transform Infrared (FTIR) gas analyser in a closed *in situ* chamber technique with incubation times of 30 minutes (10 second acquisitions). Each chamber was inserted into the soil to a depth of approximately 10 cm (with and without tussock grass) and remained *in situ* during the remediation process. Baseline (pre-treatment) gas emission data was collected from plots in fuel contaminated areas (with and without tussock grass), and compared with corresponding emissions post nutrient and air-sparge treatment. The measurement of gas fluxes allows the evaluation of efficacy of *in situ* remediation of hydrocarbons in soils at Macquarie Island. Corresponding soil core samples at two depths (50-150 mm and 200-300 mm) were collected in areas with and without tussock grass pre- and post-treatment. Microbial assays were used to measure abundance and activity of soil microbial communities with and without tussock grass, before and after treatment.

RESULTS AND DISCUSSION

Accurate *in situ* gas flux measurements were successfully obtained using FTIR in this closed system configuration across the affected site. This is the first example of FTIR application to site remediation in extreme environments. Gas flux measurements showed no significant change ($p > 0.05$) after nutrient addition and air sparging at this early stage of remediation. However, contaminated soils with *P. foliosa* growth showed significantly lower ($p < 0.01$) CH₄ flux suggesting tussock assist in oxygenation of the soil. Further, significantly greater CO₂ flux ($p < 0.01$) in *P. foliosa* vegetated soils suggest tussock may stimulate oxidative metabolism.

Soil microbial abundance and activity measurements revealed a highly adapted population already existing in contaminated soil (compared with clean soil, $p < 0.05$) prior to the onset of treatment, and at levels typically found under mesophilic conditions. This suggests under aerobic and nutrient suitable conditions rhizoremediation is a viable option at the sub-Antarctic site. Monitoring will continue during summer months throughout the planned five year remediation program.

REFERENCES

- Deprez, P.P., Arens, M. and Locher, H. (1995) Identification and preliminary assessment of contaminated site in the Australian sub-Antarctic 2: Macquarie Island. Australian Antarctic Division, Hobart.
- Ferguson, SH., Powell, SM., Snape, I., Gibson, JAE. and Franzmann, PP. (2008) Effect of temperature on the microbial ecology of a hydrocarbon-contaminated Antarctic soil: Implications for high temperature remediation. *Cold Regions Science and Technology*, 53: 115-129.
- Gaskin, SE., Soole, KL. and Bentham, RH. (2008) Screening of Australian native grasses for rhizoremediation of aliphatic hydrocarbon contaminated soil. *International Journal of Phytoremediation*, 10: 378-389.
- Gaskin, SE. and Bentham, RH. (2010) Rhizoremediation of hydrocarbon contaminated soil using Australian native grasses. *Science of the Total Environment*, 408: 3683-3688.

CAN THE EXTENT OF TPH AND PAH BIOREMEDIATION BE PREDICTED USING BIOACCESSIBILITY ASSAYS?

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INTRODUCTION

In order to minimize the volume of waste to landfill, remediation technologies may be implemented to reduce contaminant concentrations. Bioremediation is a readily available and relatively low cost (in relation to other treatment options) remediation technique for TPH and PAH-contaminated soils. However, its current use is limited by the lack of understanding of bioremediation and the time required to reach acceptable endpoints, coupled with the extended treatment times that may be required to achieve cleanup targets and the associated actual or perceived 'delay' costs. Therefore, while bioremediation technologies are well established, the technique may be considered to be 'infeasible' on a time or budget basis due to lack of endpoint accountability. In addition, if bioremediation is implemented, it may fail to achieve cleanup targets even under optimal conditions due to limitations in contaminant bioavailability. This may result in significant expenditure, utilization of resources and time without achieving the desired result. Alternative treatment technologies may subsequently need to be implemented, or additional financial resources expended for disposal of soil to higher containment landfills.

Recently, a number of methodologies have been developed for assessing the bioaccessibility of soil borne contaminants in order to predict the endpoint of bioremediation (Dandie et al., 2010; Reid et al., 2000). The majority of work has focused on the assessment of non-exhaustive extraction methods using mild extractants. Low molecular weight primary alcohols (e.g. propanol and butanol) have been used to assess TPH and PAH bioaccessibility with a number of researchers observing correlations between extracted and biodegraded hydrocarbons. In addition, an aqueous based extraction technique, utilising hydroxypropyl- β -cyclodextrin (HPCD), has also been used for estimating the TPH and PAH bioaccessible fraction in soil. In this study, the bioaccessibility of TPHs and PAHs in contaminated soils was assessed using bioaccessibility assays in order to predict the endpoints of hydrocarbon biodegradation. These results were compared to pilot scale biodegradation data in order to determine the efficacy of endpoint predictions using the rapid, inexpensive non-exhaustive extraction methods.

METHODS

Pilot scale biodegradation studies (enhanced natural attenuation) were prepared using (a) TPH contaminated soil and (b) PAH contaminated soil (~100 kg) supplemented with nutrients to achieve a C:N:P molar ratio of 100:10:1. Biopile soils were treated for up to 12 months and monitored for changes in TPH and PAH concentration. Hydrocarbon bioaccessibility assays were conducted with contaminated soil using 1-propanol and HPCD extraction. Bioaccessible or biodegradable hydrocarbons were quantified following extraction with hexane:acetone (1:1 v/v) using a Dionex Accelerated Solvent Extractor (ASE 200). Gas chromatographic analysis of extracts and TPH / PAH standards were performed on an Agilent Technologies 7890A gas chromatogram equipped with a flame ionisation detector (GC-FID).

RESULTS AND DISCUSSION

Application of an ENA strategy to TPH and PAH contaminated soil resulted in a significant decrease in hydrocarbon concentration compared to NA alone (Figure 1). Pilot scale bioremediation of TPH contaminated soil resulted in a $46.4 \pm 2.6\%$ decrease (10185 ± 629 to 5455 ± 77 mg kg^{-1}) in $\text{C}_{10}\text{-C}_{36}$ hydrocarbons following 320 days of treatment (Figure 1A). In PAH contaminated, the concentration of 16 US EPA priority PAHs in ENA biopiles was reduced from 7767 ± 1286 mg kg^{-1} to 2250 ± 71 mg kg^{-1} following 182 days of treatment (Figure 1B). When the endpoint of biodegradation was predicted using contaminant bioaccessibility, there was no significant difference between predicted values, based on HPCD extraction, and values measured after 182 days for PAHs. However, HPCD extraction of TPH contaminated provided conservative values for TPH biodegradation, although variability was observed in predicted endpoints presumable due to soil heterogeneity.

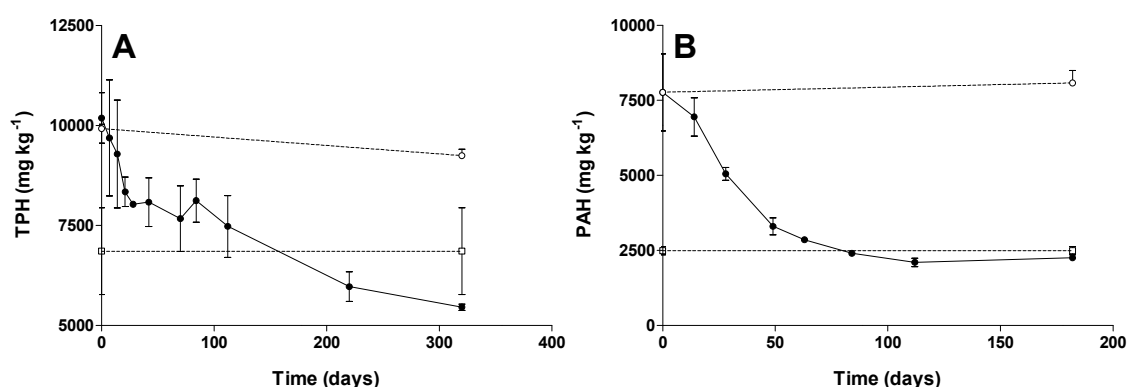


Figure 1. Pilot scale bioremediation of TPH (A) and PAH (B) contaminated soil. Changes in hydrocarbon concentration in ENA (●) and NA (○) soils are shown in addition to the predicted bioremediation endpoint based on HPCD bioaccessibility assessment (----□)

CONCLUSIONS

Assessment of hydrocarbon bioaccessibility prior to bioremediation has the potential to provide an estimate of biodegradation endpoints for TPH and PAH contaminated soils. The use of non-exhaustive extraction methods, such as HPCD, could provide a decision point on the suitability of bioremediation for soil treatment prior to implementation with minimal cost and time impacts.

REFERENCES

- Dandie, C.E., Weber, J., Aler, S., Adetutu, E.M., Ball, A.S., Juhasz A.L. (2010). Assessment of five bioaccessibility assays for predicting the efficacy of petroleum hydrocarbon biodegradation in aged contaminated soils. *Chemosphere* 81: 1061-1068.
- Reid, B.J., Stokes, J.D., Jones, K.C., Semple, K.T. (2000). Non-exhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. *Environ. Sci. Technol.* 34: 3174-3179.

HYDROLYSIS OF FENAMIPHOS AND ITS TOXIC OXIDATION PRODUCTS BY *MICROBACTERIUM* sp. IN PURE CULTURE AND GROUND WATER

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INTRODUCTION

Fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate), an organophosphorus pesticide is extensively used as a systemic and contact insecticide against soil nematodes in golf greens and horticultural crops all over the world. Generally, under environmental conditions, fenamiphos can be oxidized primarily to fenamiphos sulfoxide (FSO) followed by further oxidation to fenamiphos sulfone (FSO₂) (Cáceres et al, 2007). It has been observed that fenamiphos as well as the degradation products, fenamiphos sulfoxide and fenamiphos sulfone, may leach through the soil profile. Residues of these chemicals were found in groundwater in Florida, USA (Patrick et al., 2001) as well as in Perth, Australia (Franzmann et al., 2000). Fenamiphos has been reported to persist for several years in groundwater and the calculated half-life for its mineralization in an anaerobic aquifer in Australia was as high as 1000 years (Franzmann et al., 2000). Fenamiphos and its major degradation products are considered as highly toxic to fish, aquatic invertebrates and most terrestrial organisms. Microbial hydrolysis of organophosphorus pesticides is common and widespread in agricultural soils receiving these pesticides and several bacteria with an ability to hydrolyse these pesticides containing P-O-C bonds have been isolated and characterised. However, information on the microbial populations involved in fenamiphos degradation in soil is scant. So far there is only one report on the isolation of a pure bacterium (*Brevibacterium* sp. MM1-) able to hydrolyze fenamiphos (Megharaj et al., 2003). This study reports the isolation and characterization of a pure bacterium and its exceptional ability to hydrolyse fenamiphos and its toxic oxides in mineral medium and groundwater.

METHODS

Fenamiphos hydrolyzing bacterium was isolated from a local turf green soil (Mawson Lakes, South Australia) with a history of fenamiphos application. Based on 16S rRNA gene sequence, this bacterium was putatively identified as *Microbacterium esteraromaticum*. The efficiency of the bacterium to degrade fenamiphos and its oxidation products were tested in mineral medium and sterile groundwater by spiking the solutions with the parent compound and oxidation products followed by inoculation of the solutions with the bacterium and incubation for 24 h. Degradation of the pesticide using crude enzyme using cell-free extract was also tested, in this case an incubation period of 3 h was used. In addition, sterile controls were included in all tests. The concentration of the pesticide and its metabolites after incubation were determined using HPLC (DAD) as reported by Cáceres et al. (2007).

RESULTS AND DISCUSSION

Fenamiphos and its oxidation products FSO and FSO₂ disappeared rapidly in the medium inoculated with the bacterial culture which reached less than 2% of the spiked concentrations within 24 h after inoculation, with concomitant accumulation of respective hydrolysis products fenamiphos phenol, FSO phenol and FSO₂ phenol, in almost stoichiometric amounts (Figure 1). All three chemicals, fenamiphos, FSO and FSO₂ were stable in the uninoculated medium

during the incubation period. During the bacterial hydrolysis of fenamiphos or its oxides, there was no proliferation of the bacterium indicating this as a cometabolic process by isolate *Microbacterium* sp. The degradation of fenamiphos and its oxidation products to their respective phenols in ground water inoculated with the bacteria occurs within a 24h period. The cell-free extract of isolate *Microbacterium* sp. was highly effective in hydrolyzing fenamiphos and its oxides to their respective phenols. Within 30 minutes of inoculation, almost all the added fenamiphos, FSO and FSO₂ were hydrolyzed by the bacterium with accumulation of phenols in stoichiometric amounts. The findings of this study are of particular relevance to the environmental remediation of contaminated sites with fenamiphos and its oxidation products since these compounds have been reported to be stable in groundwater and highly toxic to aquatic invertebrates, birds and mammals (Cáceres et al., 2007; Patrick et al., 2001).

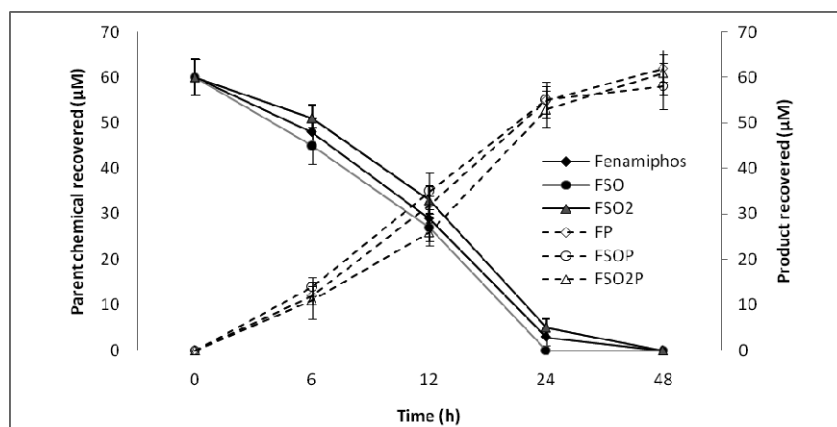


Fig. 1. Hydrolysis of fenamiphos and its oxides by isolate *Microbacterium* sp. Solid symbols represent spike chemical, while outlined symbols represent the hydrolysis products.

CONCLUSIONS

This study clearly demonstrate the exceptional ability of a novel bacterium, *Microbacterium esteraromaticum* to hydrolyse highly toxic OP pesticide fenamiphos and its oxidation products FSO and FSO₂ to less toxic phenols which are further metabolized by native microorganisms in soil and groundwater. Thus, *Microbacterium* sp. offers great potential in remediation of soil and water contaminated with pesticide waste containing fenamiphos and its toxic oxidation products.

REFERENCES

- Cáceres, T., Megharaj, M., Naidu, R (2007) Toxicity of fenamiphos and its metabolites to the Cladoceran *Daphnia carinata*: the influence of microbial degradation in natural waters. *Chemosphere* 66, 1264-1269.
- Franzmann, P., Zappia, L., Tilbury, A., Patterson, B., G., Mandelbaum, T (2000) Bioaugmentation of Atrazine and Fenamiphos impacted groundwater: Laboratory evaluation. *Biorem. J.* 4, 237-248.
- Megharaj, M., Singh, N., Kookana, R., Naidu, R. (2003) Hydrolysis of fenamiphos and its oxidation products by a soil bacterium in pure culture, soil and water. *Appl. Microbiol. Biotechnol.* 61, 252-256.
- Patrick, G., Chiri, A., Randall, D., Libelo, L., Jones, J (2001) Fenamiphos Environmental Risk Assessment. US Environmental Protection Agency. Provided for SRRD by EFED's Fenamiphos RED Team. (http://www.epa.gov/oppsrrd1/op/fenamiphos/env_risk.pdf).

BIOREMEDIATION OF GASWORKS TAR: A NE ENGLAND CASE STUDY

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INTRODUCTION

A site in North East England was used for the production of town gas for over a century. Manufactured Gasworks Plant (MGP) sites generally contain contamination including free tars, tar slurry and ammoniacal liquors with high concentrations of polycyclic aromatic hydrocarbons (PAH), monocyclic aromatic hydrocarbons (MAH, BTEX), cyanide, phenolic and heavy metal contamination.

Traditionally, during remediation of gasworks sites, tarry material was disposed of to landfill (dig and dump). This is no longer considered the best remediation technique partly due to the European Landfill Directive implementation and the increased landfill disposal charges. Numerous alternative remediation techniques have been considered and trialled, however the difficulty has been to deliver remediation of the tarry material on time, on budget and to a concentration that allows reuse of the material onsite.

BIOREMEDIATION TECHNIQUE

Our technique, Dynamic Biopiles® which is an enhanced *ex-situ* bioremediation method, provided a scientific based solution to breakdown total petroleum hydrocarbons (TPH), PAH, BTEX and phenol compounds.

Bioremediation is a well recognised process in which micro-organisms are promoted to break-down hydrocarbon based compounds. In fact, Chekol (2005) reports that biodegradation is “the most important process determining the fate of Polycyclic Aromatic Hydrocarbons (PAHs) in soil” and “is predominantly carried out by a great number of aerobic micro-organisms”. Thus there is no doubt that biodegradation (and enhanced biodegradation or bio-remediation) is an effective mechanism for breaking down PAH (and TPH) compounds, given the right conditions and ingredients.

The project was undertaken as a large commercial operation with 33,000 m³ *in-situ* (~50,000 m³ *ex-situ*) of tarry material treated and reused onsite.

RESULTS

Traditionally, enhanced bioremediation of gasworks waste has been restricted to the smaller ring PAH compounds. It can be seen on Chart 1 that in this case the rapid degradation of 2, 3 and 4 ring compounds occurred in the treated soil. The 5 and 6 ring compounds associated with Primary Gas Condensates were also remediated, however those associated with Pyrogenic Residues are not bioavailable and as such can not be remediated (eg Nakles et al, 2008; Mulvey, 2008). Leachate concentrations were successfully degraded though (Chart 2). The process clearly degraded 2, 3 and 4 ring compounds over a 6.5 month period. Due to the low concentrations (near detection limit) of 5 and 6 rings (including BaP) in the leachate these were not seen to substantially decrease over time.

Normalisation fingerprinting (Mulvey and McKay, 2005) of the PAH chemical data over time from all the stockpiles showed a change from correlation with coal tar in soil to good correlations with black carbon at the end of remediation once all tar material (Primary Gas

Condensates) had been removed. The degradation of PAH compounds by the treatment process for Total PAH ranged from 71 to 87%. The highest mean percentage reductions were observed for 2 and 3 ring compounds such as Naphthalene (94%), Acenaphthene (92%) and Fluorene (92%).

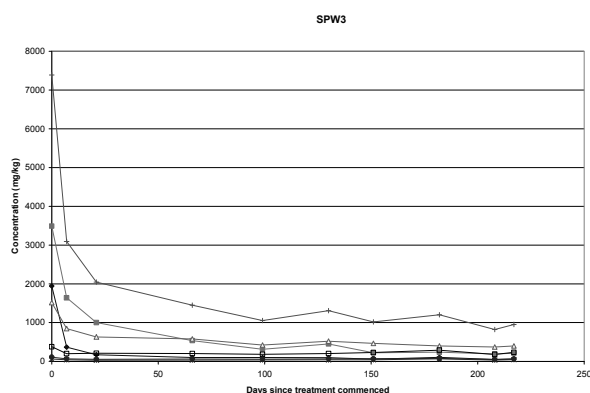


Chart 1: Total PAH soil degradation

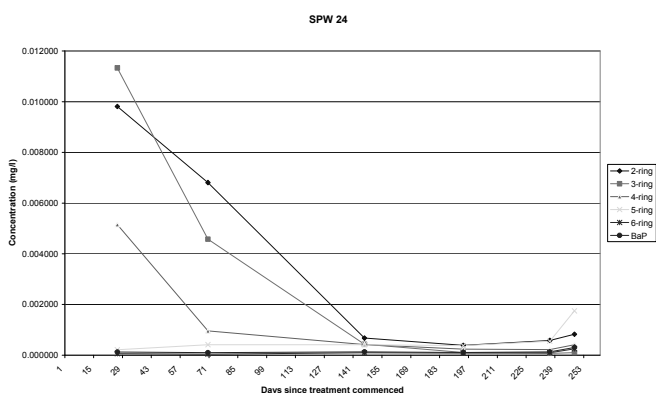


Chart 2: soil PAH leachate degradation

OUTCOME

This treatment allowed all organic wastes from the site, including the sludges from the tank bottoms, to be treated and reused with the only exception being material containing cyanide (blue billy), which was disposed off-site as hazardous waste. All bioremediated material was validated by a third party and all material was classified as meeting the site specific criteria as well as being non-hazardous (Total PAH < 1000 mg/kg). This allowed all 50,000 m³ of soil to be re-used on-site as validated clean backfill.

Our technique was assessed as the most suitable remediation method for the site by external environmental consultants and a further site specific study evaluated this technique as the most sustainable remediation technology for the tarry material (Cartwright et al., 2008). The most sustainable technology was assessed by comparing greenhouse gas emissions; intergenerational transfer; remaining liability; time; offsite infrastructure impacts; and cost. The paper concluded that not only was Enhanced Bioremediation the most economic solution for the treatment of tarry material at the site, it was also overall the most sustainable technology and had the lowest carbon dioxide emissions.

REFERENCES

- Cartwright, L., Daly, P., and Mulvey, P. (2008) Tarry Material: assessing the most sustainable remediation technology for a NE England case study. In Werner, P., Biitewski, B, and Husers, N. (Eds.) *Gasworks Europe Redevelopment, site management and contaminant issues of former MGP's and other tar oil polluted sites*.
- Chekol T. (2005) Remediation of persistent organic pollutants (POPs) in two different soils. *Remediation Journal*. 16(1) 117-139
- Mulvey P. and McKay C. (2006) Source characterization and identification as a means of assessing the type of bonding in the soil and its subsequent impact on bioavailability. *Proc MGP* 14(2), Reading, UK.
- Mulvey, 2008 The nature of bonding to black carbon – a re-evaluation of risk of MGPs. In Werner, P., Biitewski, B, and Husers, N. (Eds.) *Gasworks Europe Redevelopment, site management and contaminant issues of former MGP's and other tar oil polluted sites..*
- Nakles, D., Azzoline, N. and Kreitinger, J.P. (2008) Innovative approach for establishing remedial objectives for PAHs in Sediment. In Werner, P., Biitewski, B, and Husers, N. (Eds.) *Gasworks Europe Redevelopment, site management and contaminant issues of former MGP's and other tar oil polluted sites*.

FULL-SCALE APPLICATION OF ANAEROBIC BIOREMEDIATION TO REMEDIATE TCE IN GROUNDWATER

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INTRODUCTION

Groundwater at an active manufacturing facility in Georgia, USA was discovered to be contaminated by trichloroethene (TCE), including both overburden and shallow bedrock groundwater. Biodegradation of the TCE through reductive dechlorination was occurring based on analytical data indicating the presence of TCE daughter products cis-1,2-dichloroethene (cis-1,2-DCE); vinyl chloride (VC); and innocuous end products ethane and ethene. A corrective action plan (CAP) approved by the Georgia Department of Natural Resources Environmental Protection Division called for active in situ remediation of the suspected source area to reduce the mass of TCE and stabilize the TCE groundwater plume followed by natural attenuation to mitigate long-term risks. Enhancing the naturally-occurring anaerobic biodegradation was proposed as the potential active remediation approach based on technical and cost considerations, that it would be complementary to the proposed natural attenuation, and that it is a sustainable remediation approach relative to other more energy-intensive remediation methods.

Pilot testing was conducted in 2006 and 2007 to evaluate anaerobic bioremediation for remediating the suspected source of TCE-impacted groundwater. Pilot testing consisted of confirming the presence of *Dehalococcoides ethenogenes* (DHE) using Bio-Trap[®] samplers and Q Potential (DNA) analytical method, injecting a commercially available organic substrate through six injection points to stimulate indigenous microbes to achieve the desired anaerobic reductive dechlorination, and monitoring groundwater to evaluate remediation performance. The organic substrate was an emulsified soybean oil product combined with lactate, nutrients and buffering agents, and it was selected based on technical and cost considerations and its ability to provide a relatively long-term source of organic carbon without the need for frequent injections of additional substrate.

Pilot testing results demonstrated that anaerobic bioremediation was effective and could be applied to remediate the TCE-impacted groundwater. A full-scale application of anaerobic bioremediation was designed and implemented based on the successful pilot test results.

FULL-SCALE APPLICATION METHOD

Full-scale bioremediation included both source area treatment to address suspected sources of TCE in groundwater and a biobarrier to mitigate potential off-site migration of TCE in groundwater. A total of 70 injection wells were installed in December 2008 and substrate injections were conducted in January and February 2009. A total of 35 injection points were installed in the approximately 40m by 50m suspected source area at a spacing of 5m. The injection points were installed to the top of bedrock between 6 and 15 metres below the ground surface, and were equipped with 1.5m of well screen. The injection wells were completed at the top of the bedrock as the dissolved-phase organic carbon from the injected substrate migrated into the shallow bedrock, as determined through the pilot test and confirmed with groundwater monitoring of total organic carbon (TOC). A total of 35 injection

points were also installed to establish the biobarrier downgradient of the suspected source area along a 150m line perpendicular to groundwater flow, and the injection points were installed at the same spacing and depth as the source area injection points.

The same organic substrate solution used for pilot testing was injected into each point at a flow rate of approximately 8 to 16 litres per minute (Lpm) and a pressure of less than 200 kilopascals (kPa). This low flow and pressure helped to reduce potential short-circuiting to the surface that commonly occurs during substrate injection. Injections were accomplished using trailer-mounted system consisting of mixing tanks, injection pumps, and injection manifold equipped with valves, pressure gauges and flow meters. The total combined injection volume for all 70 injection points was approximately 380,000 litres of solution comprised of 368,000 litres of water and 12,000 litres of the organic substrate. Groundwater pumped from an unaffected bedrock monitoring well was used to provide the mixing and flushing water required for the injections, as groundwater is the best source of water because is compatible with the indigenous microorganisms.

Prior to conducting the injections, an injection risk review was completed to reduce the potential risk of the injected organic substrate from impacting other site features if it were to frac out of the ground surface. This review identified a potential risk to a nearby stormwater ditch that drains into a nearby creek. In addition to general spill prevention and secondary containment measures incorporated into the designs for these projects, measures were also take to preemptively protect the stormwater ditch and downstream creek, which consisted of controlling and limiting the injection pressure, implementing a visual monitoring program along the bank of the stormwater ditch during injections, and installing several oil-adsorbing booms along the stormwater ditch to adsorb the soybean oil product to the extent practicable. While the organic substrate itself is not dangerous, the substrate could affect aquatic life by consuming available dissolved oxygen in the surface water of the downstream creek, so the preemptive measures were warranted.

RESULTS

TCE is currently being detected in groundwater samples collected from monitoring wells in the suspected source area at the lowest concentrations since sampling began in 1993 (decreased from an average concentration of 6,000 µg/L prior to the injections down to < 5 µg/L in 2010). Rises in cis-1,2-DCE and VC concentrations were observed after TCE concentrations began decreasing, as expected, and these rises were soon followed by declining concentrations as they were also being biodegraded. Ethene was detected at concentrations as high as 120 µg/L in the source area wells, which is a significant increase over the 1 µg/L measured in groundwater samples collected prior to implementing bioremediation. These data demonstrate that enhancing the naturally occurring anaerobic biodegradation was effective and has achieved its objective.

Monitoring wells located downgradient of the biobarrier also continue to show a decreasing trend since injecting the organic substrate. Data from two of the downgradient wells also indicate the lowest TCE concentrations ever detected at those locations, including the detection of ethene, which is an indication that the biobarrier continues to remain effective several years after the initial substrate injections.

CONCLUSION

The data strongly suggest that bioremediation has effectively reduced the mass of TCE in the suspected source area and groundwater concentrations continue to decrease. Trend analysis of groundwater analytical data following the substrate injections indicates that natural attenuation without active remediation will be an effective long-term remedy to mitigate the risk associated with TCE and its daughter products in groundwater.

COMPARATIVE BIOREMEDIATION OF PETROLEUM HYDROCARBON-CONTAMINATED SOIL BY BIOSTIMULATION, BIOAUGMENTATION AND SURFACTANT ADDITION

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INTRODUCTION

The massive use and associated release of petroleum hydrocarbons into the environment over the past 200 years has resulted in a legacy of contaminated sites which require remediation. Ubiquitous soil microorganisms have tremendous potential to biodegrade hydrocarbons. Harnessing their catabolic ability to decontaminate the environment is referred to as bioremediation. This treatment method is cost effective and environmentally sound compared to traditional physico-chemical remediation approaches. As a natural process, bioremediation proceeds slowly. However, the rate of contaminant biodegradation can be enhanced by a variety of techniques (Semple et al., 2001). In this study, a bench-scale biotreatability experiment was conducted to compare the ability of different techniques including biostimulation, bioaugmentation and surfactant addition to enhance petroleum hydrocarbon bioremediation in a chronically contaminated, nutrient deficient soil. Biostimulation refers to the addition of nutrients and/or substrates to enhance the growth and activity of native microorganisms to degrade contaminants. This was tested through the addition of inorganic nutrients as well as organic amendments. The efficacy of bioaugmentation, the addition of exogenous contaminant degrading microorganisms, was tested through the addition of commercially available hydrocarbon degrading microbial cultures (Scullion, 2006). Surfactant addition was carried out to assess the ability of these compounds to solubilise, emulsify and disperse hydrophobic contaminants to overcome the problem of low contaminant bioavailability, which often precludes bioremediation (Riser-Roberts, 1998).

METHODS

A chronically contaminated (TPH>30,000mg/kg) sandy loam soil was collected from an old car service facility and prepared for treatment by homogenising and sieving (20mm). Half of the soil was spiked with creosote (1,000mg/kg), so that two soils were established: Soil 1 (TPH contamination only) and Soil 2 (TPH and PAH contamination). The soil was arranged in bench-scale biopiles. An unamended control biopile and seven treatment biopiles which all received inorganic nutrient supplementation were established for both soils. Inorganic nutrients (NH_4NO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$) were amended to attain a C:N:P ratio of 100:5:1. Biostimulation was tested through the addition of inorganic nutrients only as well as organic amendments including green waste (at 25% and 50% w/w) and a commercial product, Daramend™ (Adventus Americas Inc.). Two commercial cultures including RemActiv™ (Ziltek Pty Ltd) and Recycler 102 (Allcrobe Pty Ltd) were mixed in nutrient adjusted biopiles to assess the feasibility of bioaugmentation. A non-ionic synthetic surfactant (TERIC® G9A6, Huntsman Corporation Pty Ltd) was amended in soil with 25% (w/w) green waste to assess its effect. Soil pH, moisture and aeration were controlled to optimise bioremediation. TPH concentrations were monitored for 195 days and analysed by GC-FID. PAH concentrations were determined using GC/MS in SIM and monitored for 106 days. Heterotrophic bacteria and hydrocarbon-degrading bacteria were also monitored using the plate count method. Statistical significance of data was determined using a one-way ANOVA at $p < 0.05$.

RESULTS AND DISCUSSION

Bioremediation efficiency was assessed by the reduction in soil hydrocarbon concentration. After 195 days, all treatments to differing extents enhanced the removal of TPHs compared

to the nutrient deficient controls. However, considerable TPH reduction still occurred in the control biopiles, indicating the importance of controlling soil physiochemical factors (pH, moisture and oxygen) to optimise bioremediation. Biostimulation with nutrients alone enhanced TPH removal, confirming that bioremediation is nutrient limited and that the soil possessed a well adapted hydrocarbon-degrading microbial community. Organic amendments had a further biostimulatory effect, possibly by providing additional nutrients, ameliorating soil physiochemical properties and enhancing microbial diversity. Daramend™ greatly enhanced TPH removal, particularly in soil 2 which contained a higher addition rate (3.5% w/w) compared to soil 1 (1% w/w). Green waste addition at 25% (w/w) resulted in a greater TPH removal compared to 50% (w/w) addition, signifying the importance of determining the appropriate mix ratio for bioremediation. The supplementation of exogenous contaminant degraders enhanced TPH removal in the case of RemActiv™, whilst removal efficiency was inconsistent with Recycler 102. Variable TPH removal effectiveness was observed with the surfactant in green waste amended soil. The potential of the surfactant to promote contaminant bioavailability and enhance the rate of TPH biodegradation was demonstrated; however inhibitory effects were also inferred.

A high reduction in Σ PAHs occurred in all biopiles over 106 days in Soil 2 (spiked) but differential removal efficiency between the control and treatments was unapparent. The main conclusion drawn was that spiked soils do not reflect the behavior of contaminants in genuinely polluted and weathered soil. Soil heterotrophic and hydrocarbon-degrading bacterial counts were higher in all treated biopiles compared to the controls but in general were poor indicators of bioremediation efficiency.

Table 1. Percent reductions in soil TPH and the sum of PAH compound concentration after 195 and 106 days respectively

Soil Treatment	TPH Reduction (%)		Σ PAH Reduction (%)
	Soil 1	Soil 2	Soil 2
Control	32	10	79
Nutrients Only	49	49	76*
Nutrients + 25% (w/w) green waste	50	66	80*
Nutrients + 50% (w/w) green waste	34*	59	84*
Nutrients + Daramend™	69	80	82*
Nutrients + Recycler 102	55	49	80*
Nutrients + RemActiv™	60	68	80*
Nutrients + 25% (w/w) green waste + surfactant	72	52	75*

*No statistically significant difference to the control ($p>0.05$)

CONCLUSIONS

Biostimulation, bioaugmentation and surfactant addition all showed the potential to expedite soil hydrocarbon (TPH) biodegradation in this bench-scale biotreatability study under controlled laboratory conditions. The challenge ahead is for bioremediation practitioners to demonstrate that as good or better results can be achieved in field scale soil remediation projects.

REFERENCES

- Riser-Roberts, E. (1998) *Remediation of Petroleum Contaminated Soils: Biological, Physical and Chemical Processes*. CRC Press, Boca Raton.
- Semple K.T., Reid B.J. and Fermor T.R. (2001). Impact of composting strategies on the treatment of soils contaminated with organic pollutants. *Environmental Pollution*. 112: 269-83.
- Scullion, J. (2006). Remediating polluted soils. *Naturwissenschaften*. 93: 51-65.

MICROCOSM STUDIES & ADVANCED SITE DIAGNOSTICS TO ASSESS INSITU REMEDIAL OPTIONS OF A MIXED CHLORINATED HYDROCARBON GROUNDWATER PLUME

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INTRODUCTION

When considering implementation of a full-scale *insitu* enhanced biotic or abiotic remediation technique there may be inherent difficulties in justifying the viability of its application or the use of many of the alternative amendments that are available.

This decision making has previously involved the collection of multiple rounds of data and the use of inefficient bench top microcosm studies. However as reported by Burns and others (2010) a new method of completing *insitu* microcosm studies using amendable sampling devices combined with advanced site diagnostics (ASD) can provide site specific data that can be used in the assessment and design of the selected remedial approach.

The combination of amended microcosm studies with Bio-Trap® samplers allows the use of both abiotic and molecular biological tools (collectively referred to as advanced site diagnostics) to be utilised to collect important site specific data. The data can be used to demonstrate definitively that contaminant destruction is occurring; the mechanism/s of destruction; compare the effectiveness of alternative stimulants (both biotic and abiotic); determine what microbes are present and the functional genes they are expressing.

The presentation will provide an Australian case study where the use of Bio-Trap® samplers within microcosm studies were combined with ASD to evaluate: monitored natural attenuation; biostimulation with a hydrogen release compound manufactured by Regenesys (HRC); and, stimulation of abiotic degradation pathways with a zero-valent-irons and sulfate amendment manufactured by Adventus (EHC-M), within a mixed chlorinated hydrocarbon groundwater plume.

METHODS

Deployment of two Bio-Trap® assays within the shallow and deep water bearing zones (approximately 4m and 7m below ground level respectively). Each assay consisted of 3 microcosm units: 1 MNA unit (used to assess the baseline geochemical and microbial conditions); 1 HRC unit (used to assess the effectiveness of an electron donor compound on microbial populations); and, 1 EHC unit (used to assess the effectiveness of zero-valent iron on the abiotic and biotic reductive dechlorination).

The units were left in-situ for three months to allow for integration and equilibration between the traps and the site conditions. The following conventional and ASD analysis were used:

- Geochemical fingerprint parameters including electron acceptors, dissolved gases (methane, ethene, ethane), pH and chloride production;
- Contaminants of concern (in this case chlorinated ethenes, TCE, DCE, VC and chlorobenzene (CB));
- Compound specific isotope analysis (CSIA) for TCE, DCE, VC and CB which was used to identify whether reductive dechlorination was occurring at a rate that is significantly greater in the amended units than that of the natural attenuation unit. CSIA relies on C¹² and C¹³ (both not radioactive) being consumed at different rates in the environment, which lead to a shift in the $\delta^{13}\text{C}$ (‰) for each contaminant;
- Census® and DNA analysis to determine whether specific microbes were present and the quantity of active functional genes (not only limited to Dehalococcoides spp).

Deployment of two Stable Isotope Probe (SIP) units within the shallow water bearing zone to assess and compare the effectiveness of monitored natural attenuation and enhanced bioremediation / reductive dechlorination of CB: 1 unit was used to assess the monitored natural attenuation and 1 unit was amended with zero-valent iron and sulfate (EHC-M) to assess stimulated anaerobic oxidation of CB. Two ASD methods were used to analyse the SIPs:

- Phospholipid fatty acid (PLFA) analysis. PLFA are a major component in the membranes of all microbial cells, and can unequivocally show incorporation of the contaminant into biomass; and
- Analysis of ^{13}C enriched *Dissolved Inorganic Carbon* (DIC) to demonstrate contaminant mineralisation into the aquifer.

RESULTS AND DISCUSSION

Analysis of the dataset (attached Tables 1, 2, and 3) indicates that microbial populations (which included *Dehalococcoides spp*) are low to moderate in the MNA and that the HRC and EHC amended Bio-Trap® units do not significantly increase the microbial population.

The following was noted:

- The $\delta^{13}\text{C}$ value for TCE detected in the amended units was greater than that detected in the MNA units, with the greatest increase in the EHC unit, indicating that EHC was most effective in promoting reductive dechlorination;
- Ongoing microbial mediated destruction of chlorinated ethenes and CB is occurring (i.e. the evidence of biodegradation is not remnant of past degradation that has stalled) and likely to continue to occur at a stable rate into the future. This is evident from the presence of the functional genes of *Dehalococcoides* (DHC), chlorobenzene dehydrogenase, incorporation of CB into biomass and the elevated concentrations of total organic carbon (TOC) that will continue to supply electron donors to feed the reductive attenuation process;
- Relatively high concentrations (>50 mg/L) of sulfate was detected at most locations. The highest concentrations were from units that indicated negligible growth stimulation. This indicates that sulfate may be reducing to sulfide and inhibiting *Dehalococcoides* and the reductive dechlorination processes; and
- Incorporation of ^{13}C into biomass was detected in the MNA and EHC SIP units. This confirmed that under both conditions native microbes anaerobically oxidised chlorobenzene and incorporated the carbon from the CB within their cellular structure.

CONCLUSIONS

Through the use of ASD it was established that the use of MNA or enhanced bioremediation as the sole remedial approach at the site would have limited success. Rather MNA or enhanced bioremediation could be effective as a complimentary technology used in combination with a more aggressive treatment technology, such as source area treatment, hydraulic containment or a funnel and gate system. It is considered ASD, as opposed to the traditional bench trials or full-scale field trials, has allowed for a relatively fast and cost effective evaluation of the two amendments at a microcosm scale and under *in-situ* site specific conditions.

REFERENCES

- Koenigsberg. S, Hazen. T, Peacock.A (2005). Environmental Biotechnology: A bioremediation Perspective. *Remediation* 15: 5 – 25.
- Burns. M. Myers. C (2010). Evolution of predictive tools or *in-situ* bioremediation and natural attenuation evaluations. *Remediation* 20: 5 - 16

THE INTERSECTION OF CHEMICAL OXIDATION AND BIOREMEDIATION: THE IMPACT OF PERSULFATE ON MICROBIAL POPULATIONS

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In situ chemical oxidation by activated persulfate has become a potent tool in the remediation of contaminated soil and ground water over the past four years. Persulfate can be activated by several methods, including heat, metals, peroxides and high pH, and are effective on a wide range of contaminants, including chlorinated solvents, aromatic hydrocarbons and petroleum hydrocarbons.

For the treatment of BTEX and petroleum hydrocarbons, activation of persulfate by calcium peroxide provides a unique opportunity in coupling persulfate chemical oxidation with aerobic bioremediation resulting from the continued release of oxygen from the calcium peroxide. In addition, post the oxygen release and consumption, residual sulfate generated by the reaction of persulfate and the contaminants, may be a role in anaerobic bioremediation of petroleum products via sulfate reducing bacteria. However, there has been little published work investigating the impact of activated persulfate on nascent microbial populations.

Microbial monitoring via Bio-Trap implementation in the monitoring wells before and after application of calcium peroxide – activated persulfate at a fuel transfer depot in Alberta, Canada demonstrated: 1) the efficacy of activated persulfate on BTEX, F1 and F2 fuel constituents, 2) the aerobic microbial population suffered an initial decrease in concentration during and immediately after oxidant application, 3) the microbial population completely rebounded within a month, 4) the microbial benzene utilization rate remained constant during and after application of activated persulfate.

Additional studies were conducted at Western Michigan University to investigate the impact of activated persulfate on sulfate-reducing bacteria (SRB), which are strict anaerobic bacteria, present in heavily contaminant sediments from the Kalamazoo River in Michigan, USA. The contaminants contained high levels of PCBs, PAHs and mercury. Results demonstrated that addition of strong oxidizing species does impact the SRB population concentrations immediate and post application, with a two log reduction in colony counts. However, within two months, the SRB populations were shown not only to fully recover, but to increase in concentration by two logs, even at the highest dosing of the activated persulfate. This was attributed the generation of residual sulfate concentrations from the persulfate, and the reduction of the high molecular weight contaminants into fatty acids and alcohols, both beneficial to the growth of SRBs. In addition, it was shown that the SRBs were able to convert the residual sulfate to sulfides. This provided an additional benefit with the subsequent precipitation of mercury in the sediments as mercury sulfide (cinnabar).

In conclusion, activated persulfate was shown: to be effective on petroleum hydrocarbons and PCBs; have only short term impacts on nascent microbial populations; provide beneficial impacts to sulfate reducing bacteria, thereby enhancing subsequent anaerobic bioprocesses; and to have a positive impact on metals contamination via precipitation.

ASSESSING THE APPLICATION OF ISCO IN THE SUBSURFACE

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INTRODUCTION

In-situ chemical oxidation (ISCO) was selected as the preferred remediation option for a site impacted with trichloroethene (TCE) and degradation compounds. This remedial method was considered to be suitable for the source zone in particular due to elevated concentrations in groundwater flowing in the more permeable units of the underlying quaternary deposits of interbedded sand and clay layers. For ISCO to work the oxidant needs to come into direct contact with the contaminant for the mineralisation reaction to proceed. Application of permanganate was via a 2.65% solution delivered into injection wells advanced into the upper two aquifers on the site.

Following the initial application of permanganate it was considered prudent to undertake an evaluation of the remediation works to date to allow for refinement of the application method as well as providing information to allow the estimation of rebound and the end point of remediation. In particular the estimation of the mass of TCE remaining in the subsurface and assessment of the distribution of permanganate mass were the key objectives of this stage of works.

METHODS

Visual observation was considered to be a practical method of initially assessing the distribution and persistence of permanganate in the subsurface. Groundwater monitoring has been undertaken on a quarterly basis which has allowed the assessment of dispersion and persistence of permanganate in the more permeable sand layers. Where permanganate was visually observed a sample was titrated with Sodium Thiosulfate to provide an estimation of permanganate concentration. This generally appeared to correlate well with previous assessments on other sites, which indicated that the actions of "*dispersion, diffusion, and chemical reaction, limit the observed persistence of the permanganate solution within most of the targeted aquifer zone, by one year after the injection*" (Frazier et al.). However a challenge was presented in assessing the effectiveness of the permanganate in the less permeable clay aquitards, which may represent a secondary source of TCE that could potentially create a future rebound in contaminant concentrations and thus uncertainty of ISCO as a long-term remediation solution for the site.

Soil core drilling was undertaken within the known source areas on the site, which had also been targeted heavily with permanganate injections. Soil cores were assessed under white light to allow observation of the presence of permanganate and, where present, the colour was used to estimate approximate concentration. Where fractures, fissures and clay/sand interfaces were observed the surfaces were inspected under a microscope.

RESULTS AND DISCUSSION

Groundwater monitoring bores screened within the sand units underlying the site indicated that dispersion of the permanganate was occurring in line with expectations. Bores located close to the source zone displayed high concentrations of permanganate, as this was the area of most injection, and bores located further downgradient within the TCE plume showed more dilute permanganate concentrations. Figure 1, below, shows the Sodium Thiosulfate volume used in titration as a surrogate for permanganate, which has been overlain with the

concentration of TCE in these particular monitoring bores. Permanganate is persistent in the bores for a twelve month period over which time the TCE concentrations decrease significantly.

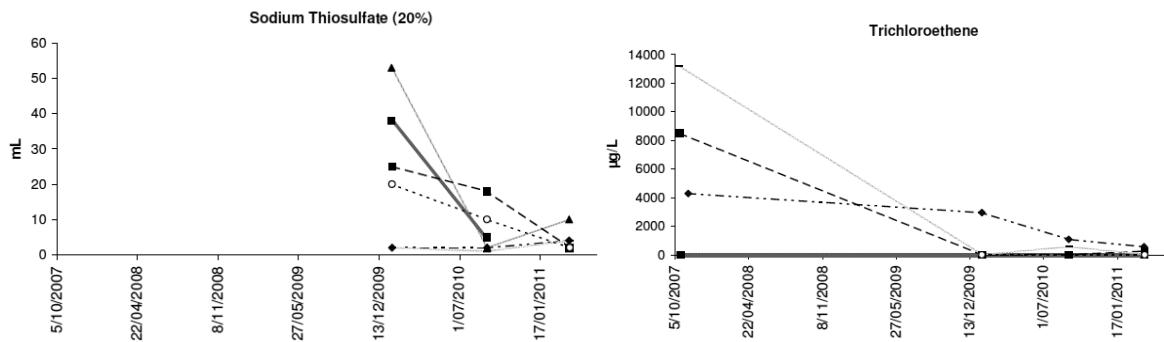


Figure 1. Sodium Thiosulfate and Trichloroethene Concentrations vs Time

Visual inspection of the soil cores demonstrated that dispersion of the permanganate within the sand layers was extensive and is likely to continue to provide oxidation potential for TCE twelve months post injection.

Microscopic inspection of the soil cores, and in particular the clay sections, indicated the presence of some permanganate within cracks and fissures that were close to sand/clay interfaces and some minor penetration of the clay matrix. There was however limited evidence that the permanganate was effective at penetrating the clay matrix significantly beyond 1-3mm.

CONCLUSIONS

The distribution of permanganate in the sand layers has been achieved to mirror the distribution of TCE on the site. This was in part due to the locations of injection selected, but importantly the dispersion of permanganate within the sands was extensive and does not appear to be selective in transmission pathways. The presence of permanganate has been demonstrated to reduce concentrations of TCE significantly and thus it is concluded that sufficient direct contact is occurring for reaction of permanganate and TCE. Persistence of the permanganate for a period of twelve months is considered to be a good sign that this reaction is still occurring a significant time post injection.

The distribution of permanganate within the clay soils has been limited to the sand/clay interfaces with some minor penetration of the clay matrix observed. This therefore reduces the ability of the permanganate to react with any TCE present within the clay soils. It is not clear yet, to what extent the TCE has penetrated the clay soils or whether it has followed a pathway of least resistance and is predominantly located within the sand layers.

Over time it will be necessary to monitor rebound concentrations of TCE in the sand layers to determine whether significant diffusion of TCE is occurring from the clay soils where the permanganate has not been able to react with TCE.

REFERENCES

Frazier J.D, Fiacco R.J, Pac T, and Lewis R (2006) *Physical Distribution and Temporal Persistence of Injected Permanganate within Saturated Soils.*

REMEDICATION OF CHLORINATED HYDROCARBON IMPACTED GROUNDWATER USING IN-SITU CHEMICAL OXIDATION (ISCO), WESTERN SUBURBS, VICTORIA

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INTRODUCTION

The subject site is located in the inner western suburbs of Melbourne on late-Tertiary aged fractured basalts of the Newer Volcanics formation. The site was used for production of foam and other materials for over 40 years, which lead to contamination of soils and groundwater within the fractured basalt by halogenated and non-halogenated (i.e. chlorinated) hydrocarbons).

In-situ chemical oxidation (ISCO) is considered as a well developed and widely used in situ remediation technology for soil and groundwater contaminated with organic compounds. The ISCO process involves injecting oxidants (substances readily reduced) and, in some instances, other reaction generating substances (catalysts) into contaminated areas of the subsurface. The oxidant reacts with the contaminant causing decomposition of the contaminant and the production of innocuous substances such as carbon dioxide and water. This reaction, called oxidation, is a chemical reaction characterised by the loss of one or more electrons from an atom or molecule. When an atom or molecule combines with oxygen, it tends to give up electrons to the oxygen in forming a chemical bond. Carbon in the form of organic carbon and manufactured hydrocarbons are common substances readily oxidised (reductants). For ISCO to effectively reduce contaminant concentrations there must be direct contact between the oxidant and the contaminant.

The primary objective of this abstract is to summarise the performance of ISCO within a fractured basalt aquifer. In particular, the oxidation breakdown process of chlorinated hydrocarbons and the occurrence of rebound as an important factor in evaluating the technology success.

METHODS

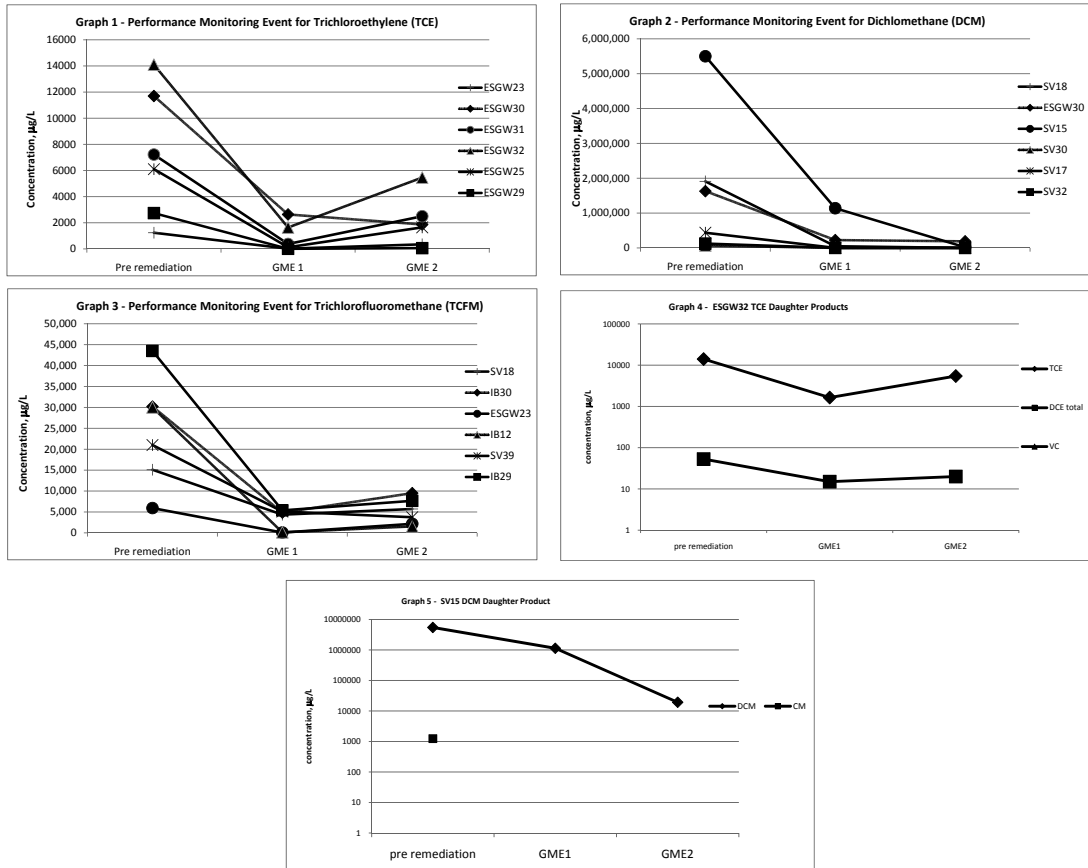
After an extensive site investigation, refinement of conceptual site model, development of an overall human health and environmental risk assessment, pilot trials and completion of a remediation feasibility study, ISCO using Modified Fenton's Reagent was selected as the appropriate technology in light of the local geology and hydrogeology, and economic and environmental impacts.

The groundwater remediation system involves an ISCO approach using a series of injection bores to deliver the required oxidant and catalyst, and installation of soil vapour extraction bores for managing residual vadose and phreatic zone vapours. The delivery system was driven using pneumatic pumps followed by low to medium pressure compressed air to disperse the Modified Fenton's Reagent through the fractures of the basalt aquifer.

Stakeholders including the EPA appointed Auditor, Victorian EPA and client have been involved right throughout the assessment phases, pilot trials, remediation feasibility and remediation stages.

RESULTS AND DISCUSSION

A pre remediation groundwater monitoring event (GME) was undertaken followed by two consecutive full scale ISCO injections and further polishing of targeted bores. The post groundwater conditions were monitored by undertaking two consecutive GME's across the



site. The results of the pre-remediation GME undertaken in November 2010 followed by two post remediation GME's (April and June 2011) are presented on Graphs 1 to 5.

Graphs 1 and 2 show significant reduction of TCE (75%), DCM (98%) and TCFM (91%) upon completion of two full scale in situ chemical injection events, with minimal rebound in selected bores. It was noted that concentrations vary dramatically across the site over short distances due to spatial variability, and consequently rebound was rapidly experienced within low permeability fractures of injection points such as bore ESGW 32. The likely by products of TCE and DCM were not evident in most of the injection bores, as shown above (see Graphs 4 and 5) with the expected by products also breaking down at the same time as the primary chemicals of concern.

CONCLUSIONS

Based on the results, it can be concluded the selected remediation technology (in situ chemical oxidation using Modified Fenton's Reagent) was appropriate in cleaning up the impacted fractured basalt aquifer with significant reduction of mass over a short period of time. The rebound observed within the low permeability fractures within selected injection bores was due to oxidants not having enough time to diffuse into the contaminant or could be attributed to extended slow mass transfer and transport mechanisms of residual contaminants. Due to the strong oxidising power of hydroxyl radicals (OH) as a result of the Modified Fenton's Reagent, the expected by products were not evident in most of the injections. Therefore, most of the chemicals of concern are likely to have undergone the complete degradation process under aerobic conditions, producing harmless substances such as carbon dioxide, water and inorganic chloride.

REFERENCES

In situ Chemical Treatment, Yin and Allen, July 1999; and Environmental Protection Authority, A Citizens Guide to Oxidation, April 2001.

IN-SITU CHEMICAL OXIDATION FOR REMEDIATION OF PETROLEUM HYDROCARBON IMPACTED GROUNDWATER UTILISING INNOVATIVE DELIVERY AND DISPERSION METHODOLOGIES

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INTRODUCTION

Effective delivery and dispersion of chemical oxidant has been achieved utilising a combination of pressure pulse technology and vacuum extraction to treat petroleum hydrocarbon impacted groundwater beneath an area of public parkland in the Riverlands of South Australia. The project posed several distinct challenges in that the remedial goals had to be achieved quickly, safely and efficiently with minimal inconvenience to the public or detrimental impact on the environment.

KEY ASPECTS OF THE CONCEPTUAL SITE MODEL

A program of groundwater monitoring has been undertaken on and in the vicinity of a service station situated some 60 m from the banks of the River Murray. The monitoring works revealed the presence of petroleum hydrocarbon impacts to groundwater beneath public parkland between the river and the service station site which included free product in one well and significant dissolved phase impacts in a sentinel monitoring well located approximately 45 m and 20 m from the river respectively. Characterisation analysis had revealed the product to comprise degraded leaded petrol. The shallow aquifer consisted of alluvial sands and is considered to be in direct hydraulic continuity with the River Murray.

Following consultations with the South Australian Environment Protection Authority (SA EPA), a SA EPA accredited site contamination auditor was appointed for the site, and a Detailed Risk Assessment (DRA) and Remediation Options Assessment (ROA) were prepared in general accordance with SA EPA guidelines (SA EPA, 2009).

The conceptual site model developed as part of the DRA revealed the presence of a number of current and historical potentially contaminating activities in the vicinity which could have led to the identified petroleum hydrocarbon impacts. However Reliance Petroleum accepted that historical fuel losses from their service station, prior to them taking ownership of the site, may have resulted in some or all of the groundwater contamination adjacent to the river. The key potentially complete exposure pathways identified in relation to the off-site impacts were considered to be associated with risks posed to surface water ecosystems and recreational users of the River Murray. Given the importance of the receptor to both regulators and the public Reliance decided to proactively remediate rather than increase certainty through further investigation which could have lead to unacceptable delays or even impact to the river.

REMEDIATION TECHNOLOGIES AND IMPLEMENTATION

The ROA considered a range of saturated zone source treatment technologies. It concluded that the preferred strategy to mitigate the potential risks would be to implement remediation works comprising a combination of in-situ treatment of dissolved phase contamination through application of in-situ chemical oxidation (ISCO) and multi-phase vacuum extraction (MPVE). The ISCO amendment provided a rapid means of treating dissolved phase contamination whereas the MVPE addressed localised free product impact and controlled the injection of the oxidant in such a sensitive area.

In order for ISCO to be successful the oxidant must come into contact with the contaminant for sufficient time for the oxidation reaction to occur and in such a manner that remediation workers, the general public and the environment are not put at risk. The type of oxidant and means of application is therefore critical in the treatment process.

RegenOx™ was selected as the oxidant due to its ease of application and proven effectiveness for treatment of petroleum hydrocarbons. It is a proprietary two-part chemical oxidation product which comprises a controlled-release alkaline oxidant containing sodium percarbonate complex which is activated using a proprietary multi-part catalyst. This provides an effective contaminant oxidation reaction without violent exothermic reaction.

The oxidant was injected via a series of remediation wells installed across the area of impact, perpendicular to groundwater flow direction, in order to construct a 50 m long amendment 'curtain' through the treatment area. Effective dispersion of the oxidant was achieved through the utilisation of the Wavefront™ proprietary pressure pulse technology (PPT) whereby the pressure at the injection point is cycled so that a series of "pressure waves" are impressed upon the formation, radiating from each point of application. The pressure waves create temporary dilation of the pore throats thereby enhancing the flow of injectate within the formation and facilitating a more uniform and larger radius of influence than can be achieved with traditional injection technologies (Spanos et al., 2004). Vacuum extraction at adjacent wells further enhanced the distribution of the oxidant by pulling the amendment through the formation.

In addition to the amendment 'curtain', remediation works were also focussed on the vicinity of a well where free product had been detected. A high vacuum was applied to this well via a trailer mounted MPVE unit for a few hours at a time. Extracted fluids were discharged to a pallean and disposed of off-site at a licensed liquid waste facility. RegenOx™ was also injected via remediation wells surrounding the zone of free product to treat dissolved phase petroleum hydrocarbons in this area.

The distribution of the injection fluids, during and following the injection event, was assessed by monitoring vadose zone pressures as well as the variation in water levels and water quality parameters, including dissolved oxygen concentrations, pH, redox, electrical conductivity and semi quantitative measurement of peroxide concentrations.

RESULTS OF REMEDIATION

A radius of influence extending at least 8 m from the injection points was observed during the course of the works. Post remediation works groundwater monitoring events have revealed removal of free phase groundwater impacts and significant (locally order of magnitude) reductions in concentrations of dissolved phase hydrocarbon impacts within the remediation area.

CONCLUSIONS

On the basis of the findings of the post remediation monitoring it is considered that the remediation works have been successful in mitigating immediate potential risks to receptors associated with the River Murray posed by site contamination present in the targeted areas. However some rebound is anticipated and it is accepted that there is some potential for residual contamination to be mobilised in the future. A program of ongoing groundwater monitoring is therefore in place with the implementation of a Groundwater Management Plan for the site.

REFERENCES

- South Australian Environment Protection Authority (2009) Guidelines for the assessment and remediation of groundwater contamination 71p.
- Spanos, T.J.T., Davidson, B. (2004) Pressure Pulse Technology (PPT): An innovative fluid flow technique and remedial tool. *Remediation Technologies Symposium (Rem Tech 2004), Banff Canada*

DESIGN CRITERIA OF IN-SITU CHEMICAL OXIDATION

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INTRODUCTION

In-Situ Chemical Oxidation (ISCO) is an effective technology for the remediation of soil and groundwater contaminated by a wide range of organic contaminants. Different oxidant formulations have been proposed so far, including hydrogen peroxide, permanganate, persulfate, peroxymonosulfates, ozone and more recently even peroxyacids and other organic peroxy compounds have been tested although still in lab-scale (Baciocchi et al., 2010). Among these options, oxidant formulation based on hydrogen peroxide has been widely employed in the United States for the treatment of different contaminants (hydrocarbons, PAHs, PCBs, chlorinated solvents, explosives, etc.) by the in-situ Fenton oxidation (ISFO). Although ISFO is a well established technology in the United States, the number of full-scale ISFO application in Europe is still limited.

ISFO diffusion is hindered by different constraints that can be grouped in two broad classes: technological and regulatory constraints. The former ones include the issue of hydrogen peroxide stability after injection in the subsurface, which has basically two main consequences: the entity of the radius of influence, that affects the design of the injection scheme; the production of oxygen from decomposition of hydrogen peroxide, which needs to be properly evaluated and handled to avoid safety issues during site operation. Another technological constraint is represented by the site-specific hydro-geological conditions, namely the site permeability and heterogeneity that may limit the flow rate of the oxidant solution per injection well especially in shallow aquifers. The regulatory issues clearly depend on the attitude of the national or local regulator, depending for instance on whether the site belongs or not to the list of national priority sites. Typically regulatory requirements include the by-products evaluation in monitoring plans, the development of feasibility studies aimed to optimize the oxidant dosage and delivery, the control of oxidant and plume migration, eventually by imposing physical or hydraulic confinement of the site. Both groups of constraint were considered in the development of design criteria of ISFO which are discussed in this paper making reference to a feasibility study of ISFO application.

METHODS

The developed design criteria are based on the integration of the results obtained from experimental and numerical modelling of the ISFO treatment, accounting for the technological and regulatory constraints existing in the site to be cleaned-up. The main regulatory constraint consist in the requirement to perform the injection under confined conditions, in order to avoid migration of the oxidant and/or of the contaminants outside the clean-up area. This constraint is accounted for by including also pumping wells rather than injection wells only, or eventually by assuring the presence of a hydraulic barrier on the site border downstream the injection area. The technological constraints are typically related to the hydro-geological conditions of the site, which may affect the choice of the injection and pumping flow rate to be applied in the pilot scale test and consequently the radius of influence of the oxidant.

The design criteria were applied and tested for performing an ISFO feasibility study in a former refinery site located in northern Italy and characterized by heavy hydrocarbons soil and groundwater contamination (4000-5000 mg/kg and 1000-2500 µg/L, respectively). The first step of the experimental modelling consisted in standard bench-scale batch tests, which allowed to select the most effective oxidation process (H₂O₂ in this case) and the corresponding optimal operating conditions. The data collected were also used to evaluate

ENHANCED TCE DNAPL MASS REMOVAL THROUGH SURFACTANT- AND POLYPHOSPHATE-ENHANCED PERMANGANATE OXIDATION

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INTRODUCTION

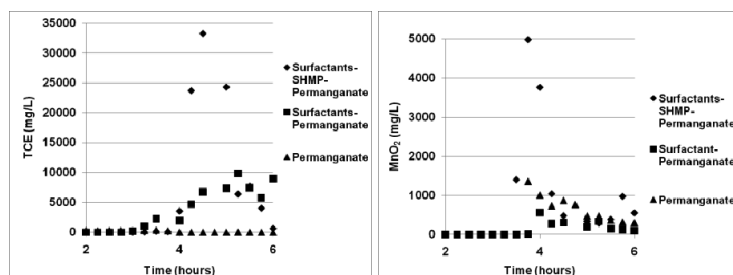
Source depletion technologies like surfactant-enhanced aquifer remediation (SEAR) and *in situ* chemical oxidation (ISCO) have shown promise for treatment of DNAPL. Surfactants can significantly enhance the solubility of DNAPL compounds (Dugan et al. 2010). One potential disadvantage of the combined SEAR-ISCO remedy is the generation of manganese dioxide (MnO_2), a by-product from permanganate oxidation that can potentially reduce subsurface permeability. The accumulation of MnO_2 could challenge the efficiency and efficacy of surfactant-enhanced permanganate ISCO of DNAPL due to decreased contact of the oxidant at the DNAPL-water interface, as well as ineffective delivery of the surfactant-permanganate flushing solution due to permeability reductions. The polyphosphate, sodium hexametaphosphate (SHMP), has previously been identified as a promising amendment to stabilize MnO_2 in solution (Crimi et al. 2009). The goal of these experimental studies was to investigate the ability of SHMP to inhibit particle deposition during surfactant-enhanced permanganate oxidation of trichloroethene (TCE) DNAPL

METHODS

Four one-dimensional (1-D) column studies with emplaced TCE DNAPL source zones were conducted: 1) water flush (control), 2) permanganate flush (0.5 wt% $NaMnO_4$), 3) surfactant-enhanced permanganate flush (1.5% surfactants + 0.5 $NaMnO_4$), and 4) surfactant and SHMP-enhanced permanganate flush (1.5% surfactants + 0.5 $NaMnO_4$ + 0.5% SHMP). Previous batch screening tests were performed with surfactants in the presence of the oxidant potassium permanganate ($KMnO_4$), to assess compatibility for coupling with $KMnO_4$ (Dugan 2008). Compatibility was defined as less than 25% of the oxidant was consumed within a 24 hour reaction period. The anionic surfactants sodium dioctyl sulfosuccinate (Aerosol OT), and sodium dodecyl sulfate (SDS) were selected for use in the column experiments. The initial NAPL saturation within the columns was 2% and the flushing flow rate was 3 mL/min. The remedial goal was to remove >90% of the TCE DNAPL mass within the columns. At the conclusion of the experiment the column contents were extracted to determine the final mass of TCE DNAPL and MnO_2 retained within each column.

RESULTS

Column experiments were conducted with and without the addition of SHMP to evaluate the effect of polyphosphates on MnO_2 deposition/retention and DNAPL mass transfer during permanganate ISCO. The TCE and MnO_2 concentrations measured in the effluent of the columns are illustrated in Figures 1a and 1b.



Figures 1a and 1b. Measured TCE and MnO_2 concentrations

The maximum TCE concentration of 34,000 mg/L was observed in the surfactant-SHMP-permanganate column indicating enhanced DNAPL mass transfer due to decreased MnO₂ formation (Figure 1a). Increased MnO₂ mobility is observed in the surfactant-SHMP-permanganate column effluent as a result of MnO₂ sequestration and stabilization (Figure 1B). Table 2 summarizes the MnO₂ data measured in the column effluents and the final mass of MnO₂ retained within each column.

Table 2. Mn as MnO₂ Data Summary

Column	MnO ₂ in effluent (g)	MnO ₂ extracted from sand (g)
Permanganate Flush	0.050	0.061
Surfactant-Permanganate Flush	0.017	0.228
Surfactant-SHMP-Permanganate Flush	0.109	0.069

The results indicate 85% more MnO₂ was measured exiting the surfactant-SHMP-permanganate compared to the surfactant-permanganate column. These results point toward enhanced mobility of the MnO₂ solids due to the addition of the sequestering reagent SHMP. In addition, 80% more MnO₂ was extracted from the porous media of the surfactant-permanganate column which suggests increased MnO₂ film formation in the source zone in the absence of the sequestering agent SHMP. Table 3 provides the performance assessment for the column experiments. Greater than 90% of the DNAPL mass was removed in the columns that had surfactants in the flushing solution. However, a greater mass of DNAPL was removed in the column containing SHMP in the flushing solution. This result would point to increased DNAPL mass transfer occurring in the surfactant-SHMP-permanganate column due to less MnO₂ film formation.

Table 3. Performance Assessment

Delivery Method	Water Flush	Permanganate flush	Surfactant-Permanganate Flush	Surfactant-SHMP-Permanganate Flush
TCE removed (%)	58%	73%	94%	>99%

CONCLUSIONS

Despite the growing toolbox of technologies and approaches for managing DNAPL sites, the use of a single remedial technology for cleanup of DNAPL-contaminated sites to typical regulatory criteria has been demonstrated to be a rare occurrence. The combined SEAR-SHMP and permanganate-ISCO remedy proposed herein aims to improve the efficiency and cost-effectiveness of DNAPL destruction by reducing time-on-site requirements, amendment costs, and/or infrastructure costs. Improved technologies for addressing DNAPL sites more cost-effectively can dramatically reduce life cycle costs for managing these sites. The experimental results indicate that inclusion of a polyphosphate into the surfactant-permanganate flushing solution could effectively enhance DNAPL mass transfer through stabilization of manganese dioxide particles.

REFERENCES

- Crimi, M. L., Quickel, M., and Ko, S. (2009). "Enhanced permanganate *in situ* chemical oxidation through MnO₂ particle stabilization: Evaluation in 1-D transport systems." *J. Contam. Hydrol.*, 105(1-2), 69-79.
- Dugan, P. J. (2008). "Coupling surfactants/cosolvents with oxidants: Effects on remediation and performance assessment," Doctor of Philosophy. Environmental Science and Engineering Division, Colorado School of Mines, Golden, Colorado.

MIMICKING NATURE: OXIDATION OF 2,4,6-TRICHLOROPHENOL WITH MIXED VALENT MANGANESE OXIDES (K-OMS-2)

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INTRODUCTION

Chlorinated phenols are widely distributed in the environment due to their use as biocides, defoliants, disinfectants, and wood and glue preservatives. 2,4,6-trichlorophenol (TCP) is a carcinogen and listed as a priority pollutant by the U.S. Environmental Protection Agency. A green method has been developed for the degradation of TCP using manganese oxide octahedral molecular sieves (K-OMS-2). Previous degradation studies of TCP have failed to break the benzene ring yielding chlorinated quinones and catechols (Olaniran, *et al.*, 2011). In this study, UV-Vis spectroscopy confirms the complete degradation of TCP in five minutes. Analysis of species adsorbed to the K-OMS-2 by DART-MS and FTIR indicates that the primary reaction intermediate has a molar mass of 74 with the functional groups C-O, C=C, and C-H, respectively. Oxidation of TCP was studied at a concentration relevant to real-world environmental site contamination (Olandiran, *et al.*, 2011). K-OMS-2 exhibits redox cycling between manganese oxidation states, mimicking the effect of microbes in the environment that require manganese as an electron acceptor for respiration. (Lovley, *et al.*, 2004). This constant cycling enables the oxidation of contaminants in mere minutes compared to the years it takes in nature.

METHODS

Green Synthesis of K-OMS-2

KMnO₄ (1.8 g) was dissolved in 70 mL of distilled deionized water (DDW) and stirred for 30 minutes to form a homogeneous solution which was further transferred into a 125 mL Teflon-lined autoclave for hydrothermal treatment at 240°C for 4 days. The resultant slurry was washed with DDW to remove any possible impurities. The product was dried in a vacuum oven at 60°C overnight.

Preparation of the TCP Colloid

Pure analytical grade TCP (98%) from Fisher was added to a solution containing the proprietary, non-ionic surfactant, VeruSOL-3[®], and DDW. Concentrations of TCP and VeruSOL-3[®] were 5 g/L and 15 g/L, respectively. Solutions were mixed in amber bottles with a magnetic stirrer for 24 hours.

Degradation of TCP with K-OMS-2

Solution Analysis

K-OMS-2 (15 mg) that was sonicated in DDW for 15 minutes was added per 536 ppm of TCP. Aliquots were periodically removed, filtered through a 0.45 micron PTFE syringe filter several times, and analysed for TCP degradation *via* UV-Vis spectroscopy

Catalyst Analysis

K-OMS-2 was separated by centrifuging for 5 min. at 5000 rpm. Reaction solution was removed with a Pasteur pipette and the K-OMS-2 was washed with DDW and dried overnight in a vacuum oven at 40°C. The K-OMS-2 was analysed for adsorbed species by both DART-MS and FTIR.

RESULTS AND DISCUSSION

TCP degradation in the aqueous phase was confirmed *via* optical absorbance measurements on a Jasco V-530 UV-Vis Spectrophotometer. A quartz cell with a path length of 1.0 cm was used for all measurements. Figure 1 shows the degradation of TCP as a function of time at its characteristic wavelength of 287 nm.

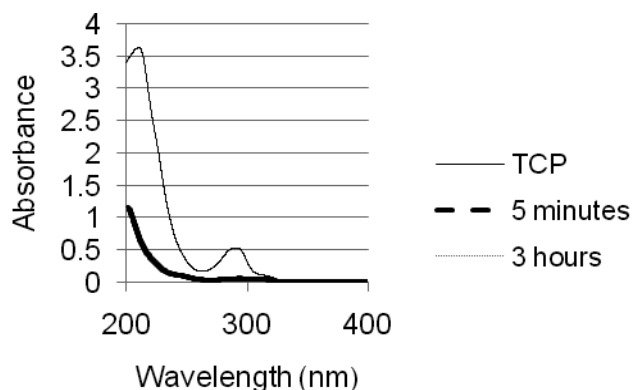


Figure 1. UV-Vis spectra demonstrate complete degradation of TCP.

FTIR analysis of the K-OMS-2 following reaction with TCP also indicates degradation of TCP. DART-MS confirms these data. The major adsorbed species is a degradation product having a molar mass of 74. In addition, there are several adsorbed species having molar masses greater than TCP indicating a radical mechanism (Ulrich, 1989). DART-MS are illustrated in Figures 2 and 3.

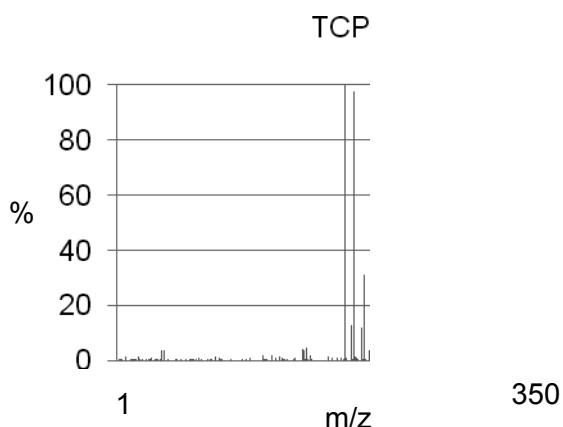


Figure 2. DART-MS of TCP

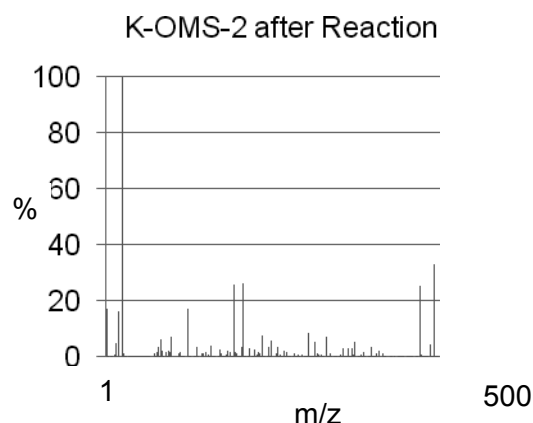


Figure 3. DART-MS of K-OMS-2 after Reaction

CONCLUSIONS

K-OMS-2 degrades TCP in just 5 minutes *via* a radical mechanism. Unlike previous studies yielding only chlorinated quinones and catechols, the major product here is compound with a molar mass of 74. IR data indicates it may be a derivative of chloroethenol.

REFERENCES

- Olaniran, A.O. and Igbinosa, E.O. (2011) Chlorophenols and other related derivatives of environmental concern: Properties, distribution and microbial degradation processes. *Chemosphere*. 83: 1297-1306.
- Lovley, D.R., Holmes, D.E. and Nevin, K.P. (2004) Dissimilatory Fe(III) and Mn(IV) reduction. *Adv. Microb. Physiol.* 49: 219-286.
- Ulrich, H.J. and Stone, A.T. (1989) Oxidation of chlorophenols adsorbed to manganese oxide surfaces. *Environ. Sci. Technol.* 23:421-428.

AN INNOVATIVE USE OF CHEMICAL OXIDATION TO TREAT PAH CONTAMINATED SOILS

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INTRODUCTION

Polycyclic Aromatic Hydrocarbon (PAH) contaminated soil is usually remediated by disposal to landfill (often following hazard reclassification). The low mobility of PAHs usually means that there are a limited number of technically feasible treatment options (e.g. onsite containment or thermal treatments), which are usually not economical when compared to landfill disposal.

This paper investigates an innovative use of chemical oxidation to treat PAH contaminated soils. Bench scale trials have been conducted and show that soils classified as Category B Prescribed Industrial Waste (EPA Victoria Publication IWRG621 *Soil Hazard Categorisation and Management*), and thus only permitted to be disposed at one landfill in Victoria (Lyndhurst), can be treated to fill material classification. This will allow beneficial reuse of the treated soils rather than disposal to landfill.

Tests are ongoing to determine if other oxidants are more effective (technically or financially) and to confirm that the process can be scaled up to field scale operation.

METHODS

The test site is located in Melbourne's northern suburbs and contains PAH contaminated soil from previous industrial uses. Previous assessment of soil at the site reported that total PAH concentrations of up to 4400 mg/kg and B(a)P concentration was up to 333 mg/kg; these concentrations are not permitted to be disposed to landfill in Victoria without prior treatment.

Two large (20 kg) soil samples were collected from the site; one sample was of the more contaminated soil and the second sample was of marginally contaminated soil. Laboratory testing showed that the first sample would classify as Category B PIW, and the second as Category C PIW. The samples were homogenised and then a 1 kg subsample was collected for treatment. The subsamples were mixed with Fenton's reagent and a surfactant and allowed to react for 7 days, before being tested again at a NATA accredited laboratory for organic contaminants.

RESULTS AND DISCUSSION

Laboratory results for the two samples are presented in Table 1. These tests conclusively show that the soil can be treated to classify as Fill Material at bench scale, which would allow unrestricted use of the soil from a contamination perspective. Initial cost estimates show that this treatment is likely to be economic when compared to landfill disposal, as well as having a lower environmental footprint.

Table 1. PAH results for pre and post treatment with chemical oxidant

	Units	Fill Material Criteria	Sample 1		Sample 2	
			Average pre-treatment concentration	Post treatment concentration	Average pre-treatment concentration	Post treatment concentration
Naphthalene	mg/kg		0.75	<0.5	<0.5	<0.5
Acenaphthylene	mg/kg		3.9	<0.5	1.7	<0.5
Acenaphthene	mg/kg		<0.5	<0.5	<0.5	<0.5
Fluorene	mg/kg		1.0	<0.5	0.9	<0.5
Phenanthrene	mg/kg		20.4	1.3	5.9	<0.5
Anthracene	mg/kg		5.6	<0.5	3.8	<0.5
Fluoranthene	mg/kg		33.2	2.5	7.6	0.5
Pyrene	mg/kg		30.1	2.2	6.7	0.6
Benz(a)anthracene	mg/kg		16.3	0.9	3.2	<0.5
Chrysene	mg/kg		13.2	0.9	2.6	<0.5
Benzo(b)fluoranthene	mg/kg		18.3	1.1	3.6	<0.5
Benzo(k)fluoranthene	mg/kg		7.0	<0.5	1.9	<0.5
Benzo(a)pyrene	mg/kg	1	15.5	0.8	3.2	<0.5
Indeno(1.2.3.cd)pyrene	mg/kg		8.1	<0.5	1.7	<0.5
Dibenz(a,h)anthracene	mg/kg		2.5	<0.5	0.9	<0.5
Benzo(g,h,i)perylene	mg/kg		9.2	0.5	2.1	<0.5
Sum PAHs	mg/kg	20	185.0	10.2	40.8	1.1

Bench scale test work is continuing to determine:

- The most effective surfactant to use. Previous work found that the use of a surfactant was essential to promote contact between the oxidant and PAH, and thus promote the chemical oxidation.
- The most effective oxidant; Activated persulfate and a sodium percarbonate reagent are being trialled. Suppliers of these reagents promote them as being more specific to organic contaminants (such as PAH & BTEX) rather than organic carbon in the soil matrix (such as plant material). In addition these reagents have less Occupational Health and Safety (OH&S) concerns than Fenton's reagent.
- Reaction time required to oxidise PAHs prior to testing and classification.
- The minimum reagent dose required to achieve treatment to Fill Material classification.

Following completion of the additional bench scale test work a high shear rotating paddle mixer (pug mill) will be used for a small field trial to confirm that the technology can be scaled up to field scale. The site contains approximately 30,000 t of PAH contaminated soil which is intended to be treated by chemical oxidation.

CONCLUSIONS

A process for chemical oxidation of organic contaminants in soil is being developed so that soils can be treated and reused rather than being disposed to landfill. This process has been successfully tested at bench scale. Preliminary data indicates that chemical oxidation will also be economic when compared to landfill disposal.

Testing is ongoing. Following completion of bench scale testing it is intended to use chemical oxidation for treatment of 30,000 t of contaminated soil at the test site.

PHOTODEGRADATION OF SURFACTANT-BASED CRUDE OIL-IN-WATER EMULSIONS

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INTRODUCTION

Crude oil-in-water (O/W) emulsions consist of dispersed crude oil droplets in a continuous phase of water (Ahmed et al., 1999), which can naturally form during an oil spill due to physical, chemical, and biological weathering. The development of surfactant-based technologies, in association with established methods for remediation of water impacted by an oil spill, is a promising new area of study. Sunlight-mediated degradation of crude oil is a natural way of cleaning crude oil pollution especially in tropical areas, in high seas where skimming would be impossible, and when chromophore-rich crude oil components are present. The development of novel photodegradation and surface-catalyzed oil degradation technologies depend on a more fundamental understanding of the photolytic degradation pathway. However, there are very few recent investigations in the literature that deal with photodegradation of crude oil or its components in natural water without the use of metal oxide catalysts and/or microorganisms. In this study, the effects of visible and UV light on the properties of stable surfactant-based crude oil emulsions were studied. Changes in emulsion properties upon reaction with light served as key indicators of degradation and enhancement of biodegradation. This study is significant in understanding the role of solar radiation in degrading spilled crude oils that form stable emulsions in the aquatic environment.

METHODS

The O/W emulsions were prepared by mixing the Prudhoe Bay (PB) and South Louisiana (SL) reference crude oils (1.0 g), VeruSOL[®]-Marine-200 (a nonionic, plant-based surfactant) (5.0 g), and synthetic seawater (1 L). These starting materials were particularly chosen due to their environmental relevance. Their compositions were carefully analysed using Nuclear Magnetic Resonance, Gas and Liquid Chromatography-Mass Spectrometric techniques.

Visible and UV light-emitting lamps were used to simulate components of natural solar radiation. Cool white ($\lambda=400-800$ nm) and monochromatic black-light ($\lambda=320$ nm) fluorescent lamps were used as constant, separate sources of visible light and UV light, respectively. Biological species, inorganic catalysts, and chemical oxidants were not utilized.

The physico-chemical properties of the emulsions were characterized providing a basis for further work concerning oil-dispersant microemulsion formation and efficiency in oil spill dispersant design. An optical microscope was used to observe the dispersed crude oil particles of emulsions. Direct observation of the emulsions in their 'natural' liquid state was also carried out using Environmental Scanning Electron Microscope (ESEM) without further dilution or sample preparation. Dynamic Light Scattering experiments were performed to determine the hydrodynamic size and distribution, and zeta potentials to assess emulsion stability. These parameters were correlated with the results of ESEM and thermal analyses (by Differential Scanning Calorimetry). The physical properties of the emulsions such as pH, conductivity, viscosity, and density were also measured. The concentrations of Ni, V, Fe, in the emulsions were analyzed using Inductively-Coupled Plasma Atomic Emission Spectrometer. UV Fluorescence spectrophotometric technique was used to monitor extent of photodegradation and formation of hydroxyl radicals.

RESULTS AND DISCUSSION

The emulsions before irradiation were stable and showed the presence of dispersed crude oil droplets in a continuous water phase and crude oil components on the water surface. Crude

oil micellization resulted in a swelling of the micelles and the formation of micro and nanoemulsions (from a few hundred nm to ~10-15 μm). The average hydrodynamic size of crude oil droplets decreased as a function of irradiation time. After 120 min irradiation, the hydrodynamic size was reduced by 13% (visible) and 58% (UV) for PB emulsions; and 27% (visible) and 42% (UV) for SL emulsions. A high degree of polydispersity of crude oil droplets in both emulsions was observed before and after irradiation. Nonionic surfactants stabilized the oil dispersed phase by repulsive interactions. UV irradiation reduced the stability of the emulsions more effectively than visible light due to photodegradation. After 120 min irradiation, the stability in terms of the magnitude of zeta potential was reduced by 14% (visible) and 38% (UV) for PB emulsions; and 6% (visible) and 14% (UV) for SL emulsions. The density of the emulsions did not significantly change but the pH values decreased drastically especially during UV irradiation. The conductivity increased as a result of formation of ionized compounds upon irradiation. The viscosity of the emulsions increased unavoidable evaporative loss of volatile contents of crude oil at ambient temperature during irradiation and formation of smaller crude oil microemulsions (more particle-particle interactions as a result of a larger interfacial area). The concentrations of Ni and Fe in PB emulsions increased after 120 min UV irradiation by as much as 1.26 and 0.323 mg L^{-1} , respectively; whereas the concentrations of V in both emulsions remained constant. This implied that metals came out of crude oil with light treatment. The emulsions were found stable toward freeze/thaw cycles and their melting temperatures generally decreased with irradiation. Polyaromatic components in crude oil were the more reactive components when subjected to visible and UV light irradiation (Fig. 1). Evidence of hydroxyl radical production existed when the emulsions were exposed to UV but not to visible light. These discernible changes in the properties of the emulsions were thus attributed to direct photodegradation and indirect photooxidation of crude oil components.

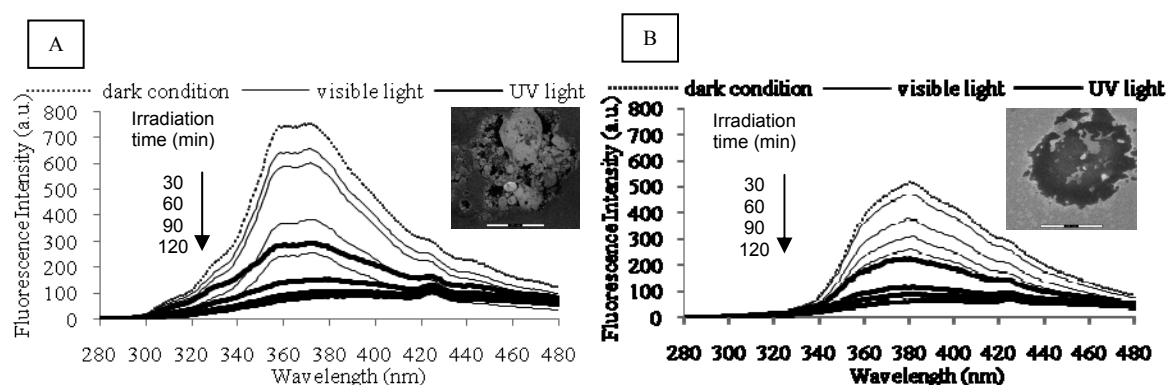


Fig. 1. UV Fluorescence emission spectra of PB (A) and SL (B) emulsions as a function of irradiation time. Insets show the ESEM images of the emulsions where crude oil components (higher intensity) are present both on the water surface and dispersed as microemulsions in the continuous phase of water (lower intensity).

CONCLUSIONS

Significant findings about the role of natural light on the degradation of crude O/W emulsions have been presented. The changes in various physico-chemical properties provided a clear explanation and a new way of assessing crude oil emulsion stability. More water-soluble photoproducts should be easily transported to and taken up by the aquatic organisms. Photodegradation of crude oil components in O/W emulsions was an effective process for mitigating some of the damaging impacts resulting from oil spills in the aquatic environment.

REFERENCES

Ahmed, N.S., Nassar, A.M., Zaki, N.N., Ghariieb, H.K. (1999) Stability and rheology of heavy crude oil-in-water emulsion stabilized by an anionic-nonionic surfactant mixture. *Petrol. Sci. Technol.* 17: 553-576.

SUSTAINED-RELEASE PERMANGANATE REACTIVE BARRIERS FOR GREEN AND SUSTAINABLE REMEDIATION OF CHLORINATED SOLVENTS

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INTRODUCTION

The intention behind site cleanup is inherently green; however, remedial activities use energy, water, and materials resources to achieve cleanup objectives. Traditional remediation technologies (e.g., pump and treat, air sparging, soil vapor extraction, or multiphase extraction) require electricity and fossil fuel to power equipment to remove contamination from soil and ground water. Extracted fluids are then processed aboveground, or disposed of in landfills when filters are used. The intractable nature of subsurface contamination suggests the need to explore the use of innovative technologies that reduce the environmental footprint of remedial treatments. Reactive materials in permeable reactive barriers (PRBs) have proven very useful for transforming or destroying organic waste *in situ*. Once emplaced they typically do not require a continued supply of electrical power and have the added benefit of creating a reactive zone for the destruction of contaminants in place. Controlled-release techniques have been utilized extensively in diverse fields such as pharmaceutical and agrochemical technologies. However, controlled- and sustained release of an oxidant during *in situ* chemical oxidation (ISCO) is an emerging concept that is extremely relevant to the field of environmental remediation, yet to-date has received little attention. ISCO using the oxidants permanganate, persulfate, and catalyzed hydrogen peroxide has shown great promise for remediation of many recalcitrant organic contaminants of concern (COC). Because the oxidant also reacts with natural organic matter, inorganic soil constituents, and other reduced compounds, the presence of a protective barrier that controls oxidant release may enhance the efficiency of ISCO and allow for long-term low-cost treatment of chlorinated solvents. To this end, sustained-release permanganate (SRP) was developed. Paraffin wax was used as the environmentally benign and biodegradable matrix material for encapsulating the solid potassium permanganate (KMnO₄) particles. The paraffin matrix protects the solid KMnO₄ particles from fast dissolution and potentially undesirable nonproductive reactions. The SRP material contains between 60%-80% permanganate and can be formed as candles for direct push applications in reactive barriers, or chipped material for hydrofracturing into low permeability media.

METHODS

One-dimensional (1-D) SRP column experiments were conducted to evaluate permanganate release behavior using deionized (DI) water as the influent or COC removal efficiency using dissolved trichloroethene (TCE) as the influent. The influent dissolved TCE concentrations were 1 mg/L and the flow rate used was 0.2 mL/min. TCE and permanganate samples were collected throughout the duration of the experiments.

RESULTS

The results of 1-D SRP column experiments with water as the influent indicate that paraffin wax effectively protected solid potassium permanganate particles from rapid dissolution. SRP release was characterized by a relatively fast initial rate followed by a significantly slower rate in the later phases (>95 days) with only ~40% of the total permanganate utilized during the operational period. Estimates of life expectancy for the SRP column with DI water influent are predicted to be 250 days at a flow rate of 1 mL/min (Figure 1).

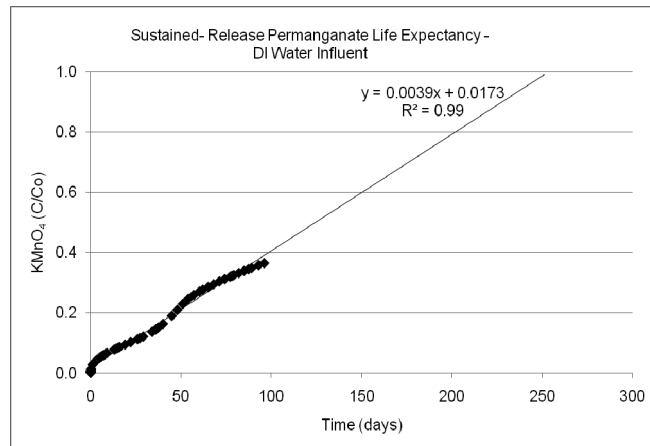


Figure 1. SRP Column with DI Water Influent Predicted Life Span

The results of 1-D SRP column studies with dissolved TCE as the influent resulted in TCE removal efficiencies ranging from 87%-100% over 166 days (Figure 2).

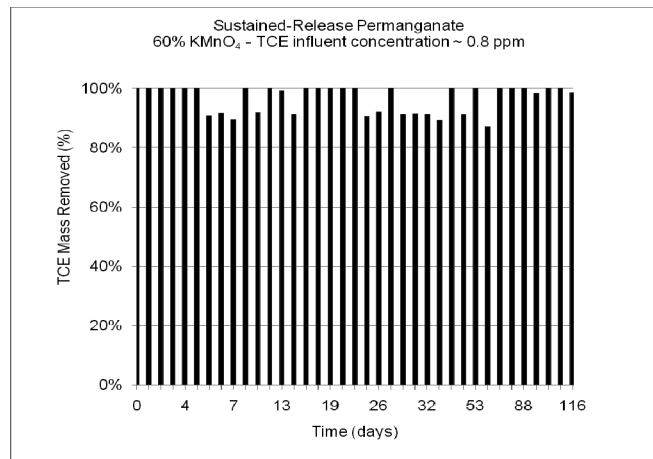


Figure 2. SRP Column with TCE Influent – Removal Efficiencies

The life expectancy of the SRP column with TCE as the influent is predicted to be 325 days at a flow rate of 0.2 mL/min.

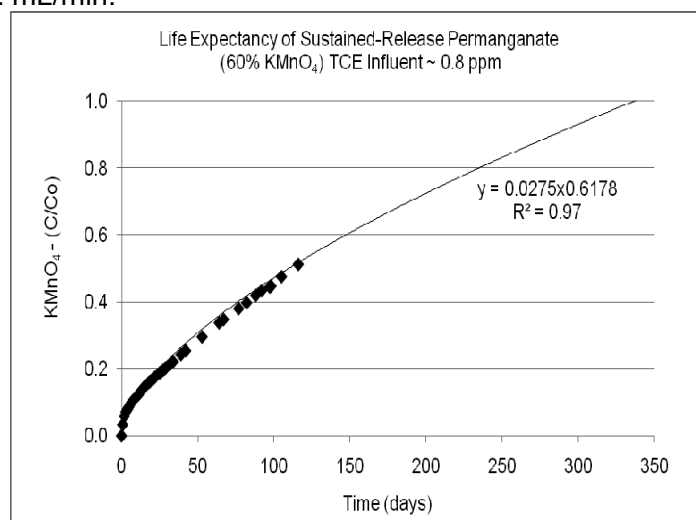


Figure 3. SRP Column with TCE Influent – Expected Life Span

These results indicate that a reactive SRP barrier could serve as a long-term low-cost passive treatment for chlorinated solvents.

CHEMICAL IMMOBILISATION OF COMPLEX CO-CONTAMINATED INDUSTRIAL WASTE

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INTRODUCTION

Waste materials contaminated with inorganic contaminants are usually remediated by chemical immobilisation where the contaminants are chemically bound in the waste as insoluble minerals. Chemical immobilisation is generally a better alternative to stabilisation or physical encapsulation (solidification), such as cement or other pozzolanic materials, as the stability of the contaminants is not dependent on maintaining the structure of the physical encapsulation. The aim of chemical immobilisation is to reduce the leachability of the contaminants in order to facilitate disposal of the waste to landfill at a reduced hazard classification.

This paper investigates the use of chemical immobilisation to treat complex industrial waste co-contaminated with high levels of seven different inorganic contaminants with a wide range of solubility characteristics.

METHODS

The waste material consists of filter cake generated from an industrial site located in Tasmania. Initial assessment of the waste material reported total and leachable contaminant concentrations well in excess of Level 3 maximum concentration values permitted for waste classification in Tasmania. Level 4 wastes are not permitted to be disposed to landfill in Tasmania without prior treatment.

Two large (20 kg) samples of the waste materials were collected from the site. The samples were homogenised and then 1 kg subsamples were collected for treatment. The subsamples were mixed with a range of different reagents and allowed to cure for 3 days before being tested again at a NATA accredited laboratory for leachable inorganic contaminants (TCLP, Toxicity Characteristic Leaching Procedure; US EPA Method 1311, 1992).

RESULTS AND DISCUSSION

Table 1. Maximum total and leachable (TCLP) concentration values permitted for waste classification in Tasmania (TAS Information Bulletin No. 105).

	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Hg mg/kg	Se mg/kg	Zn mg/kg
Level 2	200	40	2000	1200	30	50	14000
Level 3	750	400	7500	3000	110	200	50000
	TCLP As mg/L	TCLP Cd mg/L	TCLP Cu mg/L	TCLP Pb mg/L	TCLP Hg mg/L	TCLP Se mg/L	TCLP Zn mg/L
Level 2	0.5	0.1	10	0.5	0.01	0.1	25
Level 3	5	0.5	100	5	0.1	1	250

Table 2. Untreated waste total and leachable (TCLP) contaminant concentrations.

As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Hg mg/kg	Se mg/kg	Zn mg/kg
42000	970	1500	36000	22000	15000	5100
TCLP As mg/L	TCLP Cd mg/L	TCLP Cu mg/L	TCLP Pb mg/L	TCLP Hg mg/L	TCLP Se mg/L	TCLP Zn mg/L
350	3.30	0.26	4.20	<0.001	<0.05	30

Table 3. Treated waste leachable (TCLP) contaminant concentrations.

As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Hg mg/kg	Se mg/kg	Zn mg/kg
42000	1800	1800	30000	23000	9800	4400
TCLP As mg/L	TCLP Cd mg/L	TCLP Cu mg/L	TCLP Pb mg/L	TCLP Hg mg/L	TCLP Se mg/L	TCLP Zn mg/L
0.14	<0.01	<0.01	<0.01	<0.001	0.05	0.03

Maximum total and leachable (TCLP) concentration values permitted for waste classification in Tasmania are shown in Table 1. The results presented in Table 2 show that leachable contaminant concentrations in the untreated waste are above Level 3 criteria for arsenic and cadmium, and above Level 2 criteria for lead and zinc. The results presented in Table 3 are for the most effective treatment methodology, which show that all leachable contaminant concentrations in the treated waste have been reduced to below Level 2 criteria.. The leachable arsenic was reduced from 350 mg/L to 0.14 mg/L (>99.9% reduction).

CONCLUSIONS

A process for chemical immobilisation of inorganic contaminants in waste material has been developed and tested at bench-scale so that the waste material can be treated on-site and disposed to landfill at a reduced hazard classification. The chemical immobilisation process is scheduled for treatment of 3,000 tonnes of contaminated filter cake waste at the site.

REFERENCES

Department of Tourism, Arts and Environment, Tasmania, Information Bulletin No. 105, *Classification and Management of Contaminated Soil for Disposal*, August 2006.

REMOVAL OF PHENOLIC CONTAMINANTS USING SULPHATE RADICALS ACTIVATED BY SUPPORTED COBALT CATALYSTS

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INTRODUCTION

Advanced oxidation processes (AOPs) have attracted intensive interests in the wastewater treatment due to the capability of complete decomposition of organic pollutants. Active radicals are generally required to conduct AOPs. Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) reactions can provide powerful hydroxyl radicals for complete oxidation of organics. However, they are being limited by the acidic environment (pH 2–4), high amount of sludge in the coagulation, and loss of Fe ions (Shukla et al., 2010a). Recently, sulphate radicals have been proven to be of a higher oxidation potential [2.5–3.1 eV] as compared to hydroxyl radical [2.7 eV], then been proposed as an alternative (Anipsitakis et al., 2005). Cobalt catalysts have been applied to activate oxone (PMS, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) to produce sulphate radicals in either homogeneous or heterogeneous phase, however, cobalt leaching has actually become a barrier to the feasible application (Shukla et al., 2010b). In this study, various supports, such as SiO_2 , SBA-15, and activated carbon (AC) were employed to prepare supported Co catalysts for heterogeneous oxidation of phenol by the activation of sulphate radicals. The effect of Co precursors, i.e. cobalt chloride, cobalt acetate and cobalt nitrate, on the physicochemical properties of Co catalysts were investigated. Moreover, kinetic studies of the heterogeneous oxidation of phenol were carried out.

METHODS

The supported Co catalysts were prepared by an impregnation technique, in which cobalt chloride, cobalt acetate and cobalt nitrate were selected as Co precursors. SiO_2 , SBA-15, and activated carbon (AC) were used as supports. Many characterisation techniques, such as XRD, Raman, FT-IR, UV-vis, and SEM were applied to analyse the physicochemical properties of the supported Co catalysts. The catalytic oxidation of phenol was carried out in a 500 mL reactor containing 25 ppm of phenolic solution. The effects of Co-precursor, catalyst loading, reaction temperature, and oxidant dosage etc. were investigated. The phenolic concentration dependent to reaction time was analysed by a HPLC with a UV detector at wavelength of 270 nm.

RESULTS AND DISCUSSION

Firstly the effects of the Co-precursor were investigated by preparation of Co- SiO_2 (Co- SiO_2 -Cl, Co- SiO_2 -Ac, and Co- SiO_2 -Ni) using cobalt chloride, cobalt acetate and cobalt nitrate respectively. Both XRD and Raman spectra confirmed the presence of cobalt oxides in the three samples, with the influence of the cation on the formation of cobalt oxide crystalline particles. The activities and stabilities of the three samples were evaluated by the heterogeneous oxidation of phenol. The rate of phenol degradation was found to be in the order Co- SiO_2 -Cl > Co- SiO_2 -Ac > Co- SiO_2 -Ni at same Co_3O_4 loading amount of 5wt%. Co

leaching was also observed, and Co-SiO₂-Ni showed the highest stability with 4% Co leaching at second run.

The supports were also found to significantly influence the physicochemical property, activity and stability of the resulted Co catalysts. Using cobalt nitrate as Co precursor, Co-SiO₂, Co-SBA-15, and Co-AC were prepared. Co₃O₄ was found to be in Co-SiO₂ and Co-SBA-15, meanwhile Co₂O₃ was the main crystalline species in Co-AC, as proven by XRD (Zhang et al., 2010). Fig. 1 shows the efficiencies of the supported catalysts in the activation of oxone for degradation of phenol. The supports can significantly affect the efficiencies of the phenol degradation. The activated carbon showed the best performance as a support, with complete phenol removal in 30 min. This catalyst also showed excellent stability, and the activity remained unaffected even after 4-time use.

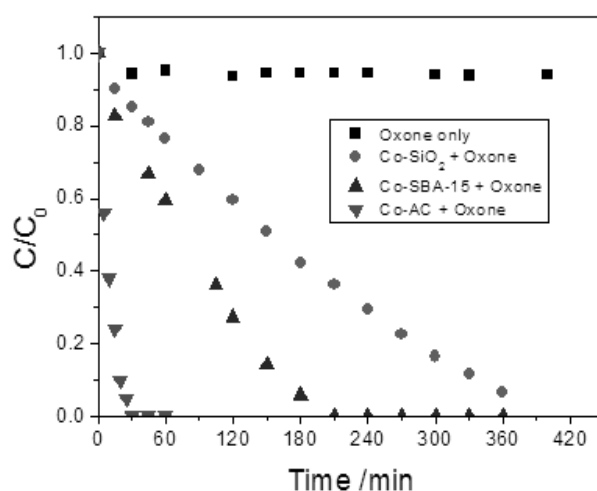


Fig.1 Degradation of phenol over various catalysts and oxone [C₀: 25 ppm, 25 °C, 0.2 g/L catalyst, 2 g/L oxone]

CONCLUSIONS

Various supported Co catalysts were prepared using different Co-precursors. The catalysts were applied to activate oxone for producing sulphate radicals for chemical oxidation of phenolic pollutants. Using same precursor of cobalt nitrate, Co-AC showed the highest activity and excellent stability. This study suggested a feasible strategy for the wastewater treatment.

REFERENCES

- Anipsitakis, G.P., Stathatos, E., Dionysiou, D.D. (2005) Heterogeneous activation of oxone using Co₃O₄. *J. Phys. Chem. B* 109: 13052-13055.
- Shukla, P., Wang, S., Sun, H., Ang, H.-M., Tade, M., (2010a) Adsorption and heterogeneous advanced oxidation of phenolic contaminants using Fe loaded mesoporous SBA-15 and H₂O₂. *Chem. Eng. J.* 164: 255-260.
- Shukla, P., Wang, S.B., Singh, K., Ang, H.M., Tade, M.O. (2010b) Cobalt exchanged zeolites for heterogeneous catalytic oxidation of phenol in the presence of peroxymonosulphate. *Appl. Catal. B-Environ.* 99: 163-169.
- Zhang, W., Tay, H.L., Lim, S.S., Wang, Y.S., Zhong, Z.Y., Xu, R. (2010) Supported cobalt oxide on MgO: Highly efficient catalysts for degradation of organic dyes in dilute solutions. *Appl. Catal. B-Environ.* 95: 93-99.

A COMPARISON OF MECHANICAL RAKE AND ULTRASONICS ON RESTRUCTURING CLAY AGGREGATES

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INTRODUCTION

More than 10 billion tonnes of tailings, which is largely made up of 90% of reusable water, are estimated to be produced globally in the mineral processing industry annually. There is increasingly pressure for mining industry to recycle and reuse the water which is trapped in the mineral tailings. The effect of the raking process in dramatically improving thickener underflow solids has been extensively studied but the structural changes in flocs and aggregates in this process are less well defined. (Du et al., 2009) found that raking dramatically changes the aggregate structure, significantly releases the inter-aggregate water by breaking the bridged flocs in the first stage of raking (usually first 10-15 min). However, after initial water release, the smaller flocs produced by raking still form strong network structures that resist further self-weight compression. Continuous raking then only rolls these smaller flocs around the rake frame without further breakage. Therefore the challenge is how to release more water from the bed during raking.

METHODS

Slurry preparation, flocculation and raking tests

50 wt. % kaolinite Q38 slurry was prepared in 0.01M KCl solution and stored in a refrigerator for overnight before use. This concentrated slurry was diluted to 2 wt. % in 0.01M KCl and mixed by a six blade stirrer at 800 rpm to ensure a vortex was produced for 30 min. 2.25L of this sample was distributed into an acrylic cylinder (90mm OD × 84mm ID, 616 mm long). Flocculant was added to the top of the slurry and mixed by 4 times blunging. After settling finished, the bed height was measured and a single rectangular rake (6 cm width × 25.5 cm length) was inserted into the settled bed and raked at a constant speed of 3 rpm for 1 h (Zbik et al., 2009).

Ultrasonic post-treatment and setup

Ultrasonic-post treatment refers to the application of ultrasonics after the addition of flocculant during kaolinite settling and consolidation processes. The detailed setup can be found in (Du et al., 2010).

RESULTS AND DISCUSSION

After flocculant addition, the fine clay particles are bridged predominantly in edge-edge (E-E) with some face-face (F-F) configurations forming separate flocs and some chain structures. When these flocs and chains settle into the hindered settling zone, the collision between flocs and chains results in the formation of the honeycomb network structure with lateral chain-like extension. This honeycomb structure traps a large amount of inter-aggregate water (Figure 1 A). The key to achieve high settled bed density is to remove the inter-aggregate water which is trapped in the honeycomb structure. During the raking process, the rake cuts a channel through the honeycomb structure, leaving a low pressure zone behind where part of the trapped water can escape (Figure 1 B). The limitation of raking is that raking can only release part of the trapped inter-aggregate water; the opened honeycomb network structure will close again after the rake passes and reforms smaller closed network structures which still trap significant amount of water (Figure 2A).

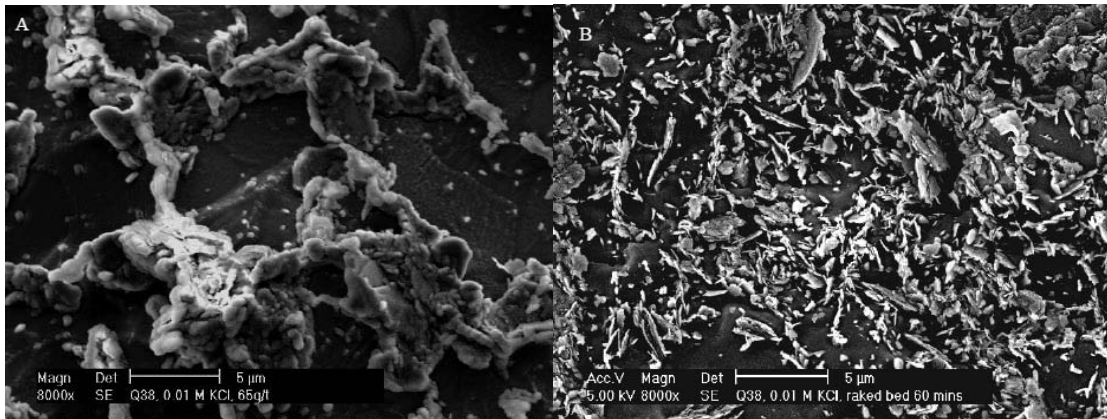


Figure 1 Bed structure in the consolidation zone before raking (A) and after raking (B) at 8 000× magnification.

To further improve the settled bed density, water must be released as much as possible before the closed network structure is formed and becomes fully consolidated. The most efficient method to improve bed density is to apply ultrasonic vibration from the bottom of the settled bed in the transition zone at a power level which can just break the self-supporting network without dispersing the aggregates (Figure 2B). The application of 2.01 W/L ultrasonic treatment in the transition zone for 2.5 min resulted in an average improvement of the bed density by 3.76 wt. % compared with raking only test, which was an 11 % improvement in settled bed density than with raking alone.

The results suggest that the application of ultrasonic in the very beginning stage of transition zone would allow more time for rake to assist water escape before the settled bed becoming fully consolidated, which should result in a bigger improvement than 11 % in settled bed density. However, this inferring needs further validation tests.

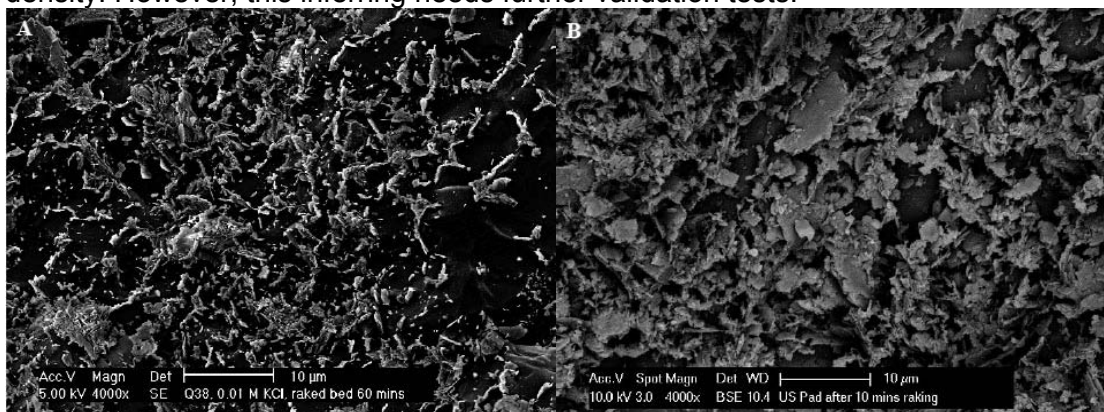


Figure 2 Cryo-SEM images at 4000× magnification of Q38 bed structure after 1 h raking by ultrasonic post-treatment of power level 2 at transition zone for 2.5 min (B) and control test with raking only (A).

REFERENCES

- Du, J., Morris, G., Pushkarova, R.A., St. C. Smart, R., (2010). Effect of Surface Structure of Kaolinite on Aggregation, Settling Rate, and Bed Density. *Langmuir*, 26(16): 13227-13235.
- Du, J., Pushkarova, R.A., Smart, R.S.C., (2009). A cryo-SEM study of aggregate and floc structure changes during clay settling and raking processes. *Inter. J. Miner. Process.*, 93(1): 66-72.
- Zbik, M.S., Du, J., Pushkarova, R.A., Smart, R.S.C., (2009). Observation of gaseous films at solid-liquid interfaces: Removal by ultrasonic action. *J. Colloid Interface Sci.*, 336(2): 616-623.

TERTIARY WATER TREATMENT PROCESS FOR CONTAMINATED GROUNDWATER

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INTRODUCTION

The Sefton Dive water treatment project forms part of the construction of the new ARTC Southern Sydney Freight Line (SSFL) that extends from Sefton to Macarthur. Enviroacific Services were engaged to undertake the water treatment works at the Sefton Dive. The dive excavation is approximately 900 m x 15 m, with the deepest point at 7 m bgl. The water treatment system has been designed to treat rainwater and groundwater entering the excavation during its construction.

Previous investigation works (EIA, 2010) indicated that water collecting in the dive would not be suitable to discharge to stormwater. The project objective was to dispose of the water via the most economical means, within the restricted work environment of the rail corridor and within programme. The two most feasible options based on these three objectives were determined to be on-site treatment with subsequent discharge to stormwater or off-site tanker disposal. Groundwater sits approximately 4 m bgl and contains elevated turbidity, total dissolved solids (TDS), total suspended solids (TSS), total nitrogen, total phosphorus, iron, chromium, copper, lead, nickel and zinc. A hydrogeological study (EIA, 2010) predicted that approximately 213 kL/day of contaminated groundwater will be encountered during the initial phase of the excavation and that the groundwater flow rate will gradually decrease over time. Based on this, the water treatment system was designed to run at 3 L/s, treating up to 238 kL of raw water in a 24 hr period. Raw water storage capacity of 159 kL has also been incorporated into the design to allow for heavy rainfall events.

It was expected that most of the contaminants would be attached to the sediments and could be removed by coagulation, flocculation and filtration/absorption processes. The contaminated sludge is removed by off-site tanker disposal and accounts for approximately 10% of overall project costs. The removal efficiency of the system was designed to process water with 75% suitable for discharge to stormwater. The remaining 25% concentrated brine is stored on-site for subsequent off-site disposal as the system was not designed to accommodate re-circulation of the concentrated brine.

METHODS

Raw wastewater was collected from the site and treated by SAS Water Solutions with a range of coagulants and polymers at varying pH values. The best visually performing combination was selected for analysis of pH, TDS, TSS, ferrous iron, chromium, copper, lead, nickel, zinc, mercury and aluminium. Samples of the raw water (as received) and treated water were submitted to a laboratory for analysis. Based on the results from the bench-scale trials and laboratory testing, the treatment system was designed to contain the following primary, secondary and tertiary components (Fig. 1):

Primary Treatment:

1. On-site Detention Tanks
2. Coagulation
3. Flocculation
4. pH Adjustment
5. Sedimentation

Secondary Treatment:

6. Sand/Zeolite Filtration
7. GAC Absorption

Tertiary Treatment:

8. Cartridge Filtration
9. Reverse Osmosis (RO) Filtration

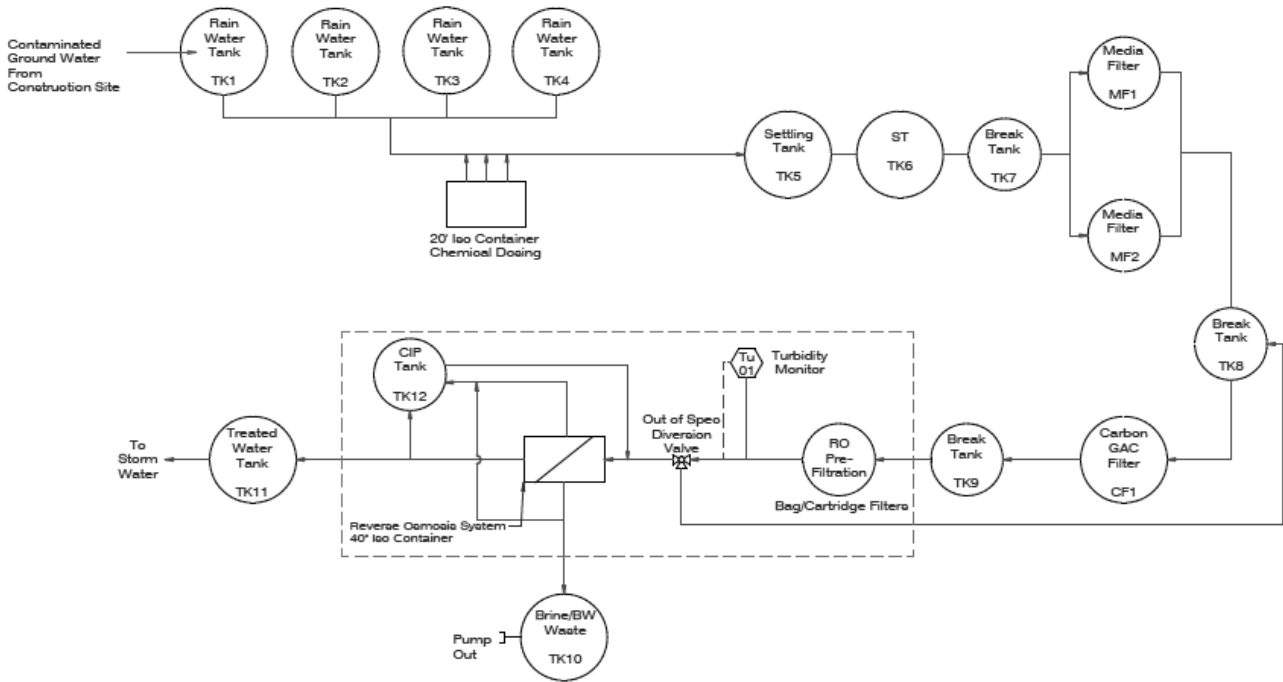


Fig. 1. Process flow diagram of tertiary water treatment system.

RESULTS AND DISCUSSION

Table 1. Untreated water contaminant concentrations.

Turbidity NTU	TDS mg/L	Total N mg/L	Total P mg/L	Fe mg/L	Cr mg/L	Cu mg/L	Pb mg/L	Ni mg/L	Zn mg/L
>1000	4300	4.6	33	1390	0.89	4.0	1.6	2.3	7.0

Table 2. Treated water contaminant concentrations.

Turbidity NTU	TDS mg/L	Total N mg/L	Total P mg/L	Fe mg/L	Cr mg/L	Cu mg/L	Pb mg/L	Ni mg/L	Zn mg/L
<0.1	46	0.1	<0.05	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001

The results presented in Tables 1 and 2 above for the untreated and treated water contaminant concentrations show the tertiary water treatment process is highly effective in reducing the contaminant concentrations. For example, TDS were reduced from 4300 mg/L to 46 mg/L (99% removal efficiency).

CONCLUSIONS

The tertiary water treatment process was able to successfully treat contaminated water from the Sefton Dive excavation to enable discharge to the stormwater system. The cost of on-site water treatment is approximately five times less expensive than off-site tanker disposal.

REFERENCES

Environmental Investigations Australia Pty Ltd, Report No. E1167.1BC (2010) South Sydney Freight Line Hydrogeological Study, Sefton Dive, Birrong, NSW.

SYNTHESIS AND CHARACTERIZATION OF THIOLATED CHITOSAN BEADS FOR Cu(II) and Cd(II) WASTEWATER REMEDIATION

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INTRODUCTION

Chitosan has been used in wastewater treatment as coagulant and adsorbent for organic and inorganic pollutants (Renault et al. 2009). The metal removal ability of chitosan is due to extensive network of C₂ amine groups (-NH₂) and C₆ hydroxyl groups (-OH) which works either by complexation, chelation or adsorption (Juang & Shao 2002). However, most toxic or precious trace metals with different chemical properties may have relatively weak interactions with unmodified chitosan. According to the Pearson Hard Soft Acid Base concept (HSAB), amine and hydroxyl groups which are hard bases may not form strong interaction with soft heavy metals such as Cd(II). In order to enhance adsorption selectivity for heavy metals, sulphur containing 'soft' functional groups such as dithiocarbamate (-HN-CS₂⁻) (Muzzarelli et al. 1982), xanthate (-O-CS₂⁻) (Sankararamakrishnan & Sanghi 2006) and thiourea (-HN-CS-NH-) (Gavilan et al. 2009) were introduced to chitosan structure. By using thiolated porous chitosan beads, treatment of wastewater in a continuous flow reactor can be enhanced. Potential formation of disulphide or thioamide crosslinks improve stability of chitosan beads, thus minimising pore clogging and maintaining flow of wastewater during treatment. In this study, thiolated chitosan beads were synthesised and characterised to investigate their potential use as Cu(II) and Cd(II) sorbent for wastewater treatment.

METHODS

Chitosan beads made by phase inversion of chitosan acetate solutions were neutralised and soaked in a mixture of ethanol and carbon disulphide for 7 days. All beads were rinsed thoroughly with ethanol and distilled water. The sulphur content was determined using LECO sulphur elemental analyser and EDAX spectrometry. The surface and core morphology was studied using CT scanner and Scanning Electron Microscopy while the BET surface area was determined using Micrometrics Gemini. The DRIFT FTIR spectra were obtained using Perkin Elmer Spectrum400.

RESULTS AND DISCUSSION

The sulphur content of thiolated chitosan beads (EDTCB) determined by LECO analyser was 7.88%. The thiolation process has increased the BET surface area of chitosan beads from 39.49 to 46.29m²/g. The mean pore aperture of EDCTB was 182.4nm, which is categorised as macroporous material. The internal structure of EDTCB consisted of multiple porous layers with most cavities located near the surface of the bead (Fig. 1.). The surface and core pore structures of EDTCB were also similar (Fig. 1.) with a sulphur content of 6.8% and 7.0% respectively. Analysis of DRIFT FTIR spectra of EDTCB found a new shoulder at 1594cm⁻¹, which is assigned to interaction of C=S stretching with C-N stretching vibrations of thiourea moiety (Gavilan et al. 2009). The presence of sulphur was confirmed by XPS spectra where a peak was detected at 163eV.

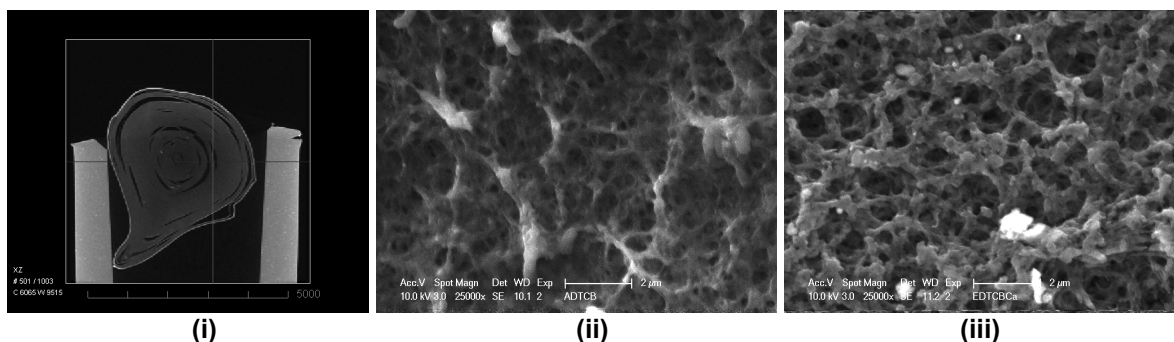


Fig. 1. CT image (i) surface SEM (ii) and cross-sectioned SEM (iii) micrographs of EDTCB bead.

The Cu(II) and Cd(II) uptake of chitosan and EDTCB beads at various sorbent dosage was conducted using 30mL of 1.0mmol/L of metal nitrate solutions (pH 5) at 25°C for 5000 minutes. As shown in Fig. 2, the Cu(II) ion uptake by EDTCB beads was slightly higher than chitosan beads at 2.0g/L dosage. However, Cd(II) ion removal of EDTCB was enhanced to 79%, as compared to 8% by pristine chitosan.

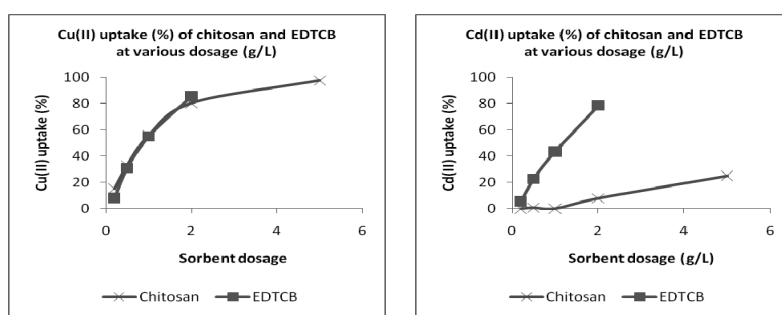


Fig. 2. Plots of Cu(II) and Cd(II) uptake (%) by chitosan beads and EDTCB against sorbent dosage (g/L).

CONCLUSIONS

New thiourea groups were introduced to chitosan beads with a sulphur content of 7.88%. The structure of thiolated chitosan (EDTCB) is macroporous with BET surface area of 46.29m²/g. Sorption of Cd(II) ion by EDTCB was improved by 10 times, compared to pristine chitosan.

REFERENCES

- Gavilan, K.C., Pestov, A.V., Garcia, H.M., Yatluk, Y., Roussy, J. and Guibal, E. (2009) Mercury sorption on a thiocarbamoyl derivative of chitosan. *J. Hazard. Mater.* 165, 1-3: 415-426.
- Juang, R.-S. and Shao, H.-J. (2002) A simplified equilibrium model for sorption of heavy metal ions from aqueous solutions on chitosan. *Water Research.* 36, 12: 2999-3008.
- Muzzarelli, R.A.A., Tanfani, F., Mariotti, S. and Emanuelli, M. (1982) Preparation and characteristic properties of dithiocarbamate chitosan, a chelating polymer. *Carbohydrate Research.* 104, 2: 235-243.
- Renault, F., Sancey, B., Badot, P.M. and Crini, G. (2009) Chitosan for coagulation/flocculation processes - An eco-friendly approach. *European Polymer Journal.* 45, 5: 1337-1348.
- Sankaramakrishnan, N. and Sanghi, R. (2006) Preparation and characterization of a novel xanthated chitosan. *Carbohydr. Polym.* 66, 2: 160-167.

VISIBLE LIGHT PHOTOCATALYTIC DECOMPOSITION OF TOLUENE WITH BiMO₄ (M = Ta, Nb)

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INTRODUCTION

Nowadays, most of human life spends in indoor environment, where exposure to some volatile organic compounds (VOCs) is highly vulnerable and produces extremely fatal diseases[1]. Since indoor environment is more polluted and has very large contents of various toxic compounds than the outdoor environment, it is extremely important to eradicate these hazardous compounds from indoor environment[2]. Various techniques and methodologies have been introduced and are in use to reduce the amount of indoor pollutants and their prevailing effect on human life. However, advanced oxidation processes like photocatalysis are proven to be helpful in decomposition of VOCs both in water and air. Although TiO₂ [3] has been extensively investigated, however, development of visible light active photocatalytic material is still very limited. Various types of niobates and tantalates have been found to be good photocatalysts for water splitting under ultraviolet and visible light irradiation[4]. Being non-toxic and highly useful, bismuth containing compounds have been widely used in clinics, cosmetics and treatment of various infections. In this study, we will report a novel and facile synthesis of bismuth tantalates (BiTaO₄) and bismuth niobates (BiNbO₄) and their applications in decomposition of toluene under solar radiations.

METHODS

A wet-chemical technique was used to synthesize BiTaO₄ and BiNbO₄. All chemicals were obtained from Sigma-Aldrich and were used without any further purification. Bismuth nitrate (10 mmole) was first dissolved in 50 ml ethanol at 60°C to make solution A. Then tantalum chloride or niobium chloride (8 mmole) was separately dissolved in 50 ml ethanol at 60°C to get solution B. Solutions A and B (either tantalum chloride or niobium chloride) were mixed while one ml nitric acid was added to the mixture, which was then continuously stirred and refluxed at 80°C for 6 hours. The mixture was aged for 12 hours at room temperature, dried in an oven at 70°C. The dried product was ground and calcined at high temperatures (700°C) for 50 hours to get the final product of BiTaO₄ and BiNbO₄. Both the materials were characterized through UV/Visible spectroscopy, XRD, SEM and EDX.

Photocatalytic tests were conducted in an air tight and enclosed stainless steel reactor fitted with gas inlet and outlet and a quartz sheet on the top to allow light into the reactor. Known amount of 300 mg of photocatalyst was evenly spread in a small petri-dish, by mixing them in 10 ml water via sonication. The evenly dispersed photocatalyst material was dried in the oven at 100°C overnight to insure complete removal of water.

RESULTS AND DISCUSSION

X-ray diffraction analyses of both the samples showed that the diffraction patterns of each material are exactly matched with that reported by other researchers. Photocatalytic activities of these materials were evaluated with decomposition of toluene in gaseous form irradiated with visible light. Xenon, 300 watt lamp was used as light source which has light intensities of 260 W/m² and 2500 W/m² in wavelength ranges below 400 nm and above 400nm respectively. It was found that the pristine BiNbO₄ could decompose toluene faster than BiTaO₄. It was also found that, under the similar conditions, a commercially known photocatalyst (TiO₂-P25) could not decompose toluene gas while both BiTaO₄ and BiNbO₄

have better photocatalytic activities. Further study has shown that BiTaO₄ had a very long life time and could be used repeatedly with minor deactivation in performance. Although BiNbO₄ showed better performance in the first time, but its activity was reduced significantly in second-round test. As shown in the figure below, both materials have almost similar performance within the first three hours; however, BiTaO₄ has lower activity than BiNbO₄ for the rest of time. After the test for the photocatalytic reaction, a color change from light yellow to dark grey was observed on BiNbO₄. However, the color of BiTaO₄ was found to be the same, suggesting stability of this material. Further investigation on these materials and their photocatalytic performance is still in progress in order to improve the photocatalytic efficiency of these compounds.

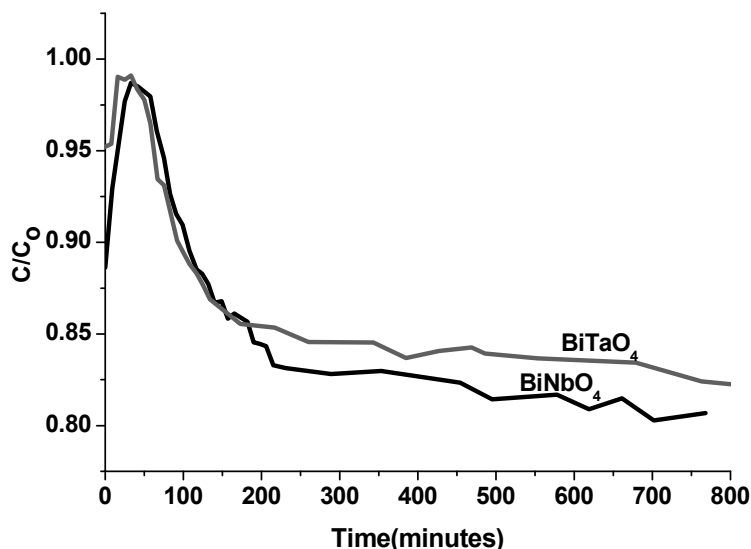


Fig.1. Photocatalytic decomposition of toluene with BiMO₄ (M=Ta, Nb) under visible light irradiation.

CONCLUSIONS

It can be concluded that both BiNbO₄ and BiTaO₄ can be easily prepared by a solution method, which is an environmentally friendly technique. BiNbO₄ has better performance than BiTaO₄, but it lacks of re-usability. Comparing with TiO₂, both materials are found to have better performance for toluene decomposition under visible light. We suggest that doping BiNbO₄ with other metals ions may be helpful to enhance its photocatalytic activity.

REFERENCES

- [1] Wang, S., H.M. Ang, and M.O. Tade, *Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art*. Environment International, 2007. 33(5): p. 694-705.
- [2] Mølhav, L. and M. Thorsen, *A model for investigations of ventilation systems as sources for volatile organic compounds in indoor climate*. Atmospheric Environment. Part A. General Topics, 1991. 25(2): p. 241-249.
- [3] Pichat, P., et al., *Purification/deodorization of indoor air and gaseous effluents by TiO₂ photocatalysis*. Catalysis Today, 2000. 63(2-4): p. 363-369.
- [4] Zhang, G., et al., *Preparation of nanosized Bi₃NbO₇ and its visible-light photocatalytic property*. Journal of Hazardous Materials, 2009. 172(2-3): p. 986-992

BACK TO BASICS – IS YOUR SITE ASSESSMENT / REMEDIATION PROGRAM BASED ON SOUND KNOWLEDGE?

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Despite the stipulation by numerous Australian guidance documents, including the NEPM, Australian Standard AS4482.1-2005 and Auditor guidelines for various jurisdictions, that the first stage of a site contamination assessment program should comprise a comprehensive site history investigation, this stage is still often excluded or rudimentary at best. However, without sound knowledge of the history of the site, including the identification of past land use practices, potentially contaminating activities and, by inference, potential contaminants, the subsequent assessment and/or remediation programs(s) may be seriously flawed.

Numerous sources of historical data are available and no single research methodology will suit every site. However, a basic list of sources should always be accessed and, depending on factors such as site location and the timing of its initial development, additional data sources researched to maximise knowledge of the site history. This, in turn, will assist in the development of an appropriate conceptual site model prior to design and commencement of an intrusive site investigation program.

This poster presents a visual comparison of complete versus incomplete historical data and demonstrates how fundamental site information can be missed or misinterpreted if the initial stage of site history research is either omitted or insufficient. It includes examples of misinterpretations based on a failure to access readily available information, including:

- incomplete Certificate of Title search (common for oil company sites) – historical land uses and potentially contaminating activities not identified
- inappropriate temporal gaps in historical aerial photograph set – previously cleared areas of bushland site subject to potentially contaminating activities not identified prior to initial mobilisation to remote site, thereby resulting in additional costs and time on project
- publically available historical maps not accessed – former location of nearby gasworks site not identified resulting in selection of inappropriate groundwater analytes
- state or national archive information not obtained – historical plans of current residential site revealed former WWII depot, including landfill, that was not previously identified
- too much faith placed on (unreliable) anecdotal information – former landfill found to be an order of magnitude greater in area than expected, thereby necessitating far greater remediation costs
- available on-line historical photographs (state photographic collection) not accessed – significant historical usage of site not identified and inadequate site assessment program undertaken
- historical dangerous good records not requested – former (disused) underground fuel storage facilities recorded on accessible plans held by government department not identified and infrastructure discovered by chance during site remediation program

REFERENCES

- Department of Environment and Conservation NSW (2006) *Guidelines for the NSW Site Auditor Scheme* (2nd edition), April 2006.
- Department of Environment and Conservation WA (2009) *Contaminated Sites Auditors: Guidelines for Accreditation, Conduct and Reporting*. Contaminated Site Management Series, November 2009.
- Environment Protection Authority Victoria (2007) *Environmental Auditor (Contaminated Land) Guidelines for the Issue of Certificates and Statements of Environmental Audit*. Publication 759.1, September 2007.
- NEPM (1999) Guideline on Data Collection, *Sample Design and Reporting*. National Environment Protection (Assessment of Site Contamination) Measure Schedule B(2). National Environment Protection Council, Australia.
- South Australian Environment Protection Authority (2009) *Guidelines for the Site Contamination Audit System*. January 2009.
- Standards Australia (2005) *Guide to the Sampling and Investigation of Potentially Contaminated Soil Part 1: Non-Volatile and Semi-Volatile Compounds*. AS4482.1-2005 Homebush NSW.

PROFICIENCY TESTING OF PESTICIDES AND HYDROCARBON POLLUTANTS IN WATER AND SOIL: REVIEW OF RECENT RESULTS

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INTRODUCTION

The National Measurement Institute (NMI) has been conducting interlaboratory proficiency testing of the identification and measurement of pesticides and hydrocarbon pollutants in soil and water for over ten years. Laboratories in Australia, Asia, and Africa have participated. Pesticides studied include organophosphate, organochlorine, and synthetic pyrethroid insecticides; and triazine, glyphosate, phenoxy acid and sulphonylurea herbicides. Hydrocarbons studied include diesel and gasoline fuels and BTEX (benzene, toluene, ethylbenzene and xylenes).

METHODS

Water from a Sydney watercourse was spiked with selected organic pollutants. Participant laboratories measured the pollutants using their normal test methods. Results from individual laboratories were compared to the robust average. Study protocols complied with the international standard ISO 17043.

RESULTS AND DISCUSSION

Recently completed proficiency studies are reported, and the results reported by laboratories placed into the context of fitness for purpose. Figure 1 illustrates typical between laboratory variation for the analysis of pesticide pollutants in water. Figure 2 illustrates typical between laboratory variation for hydrocarbon pollutants in water.

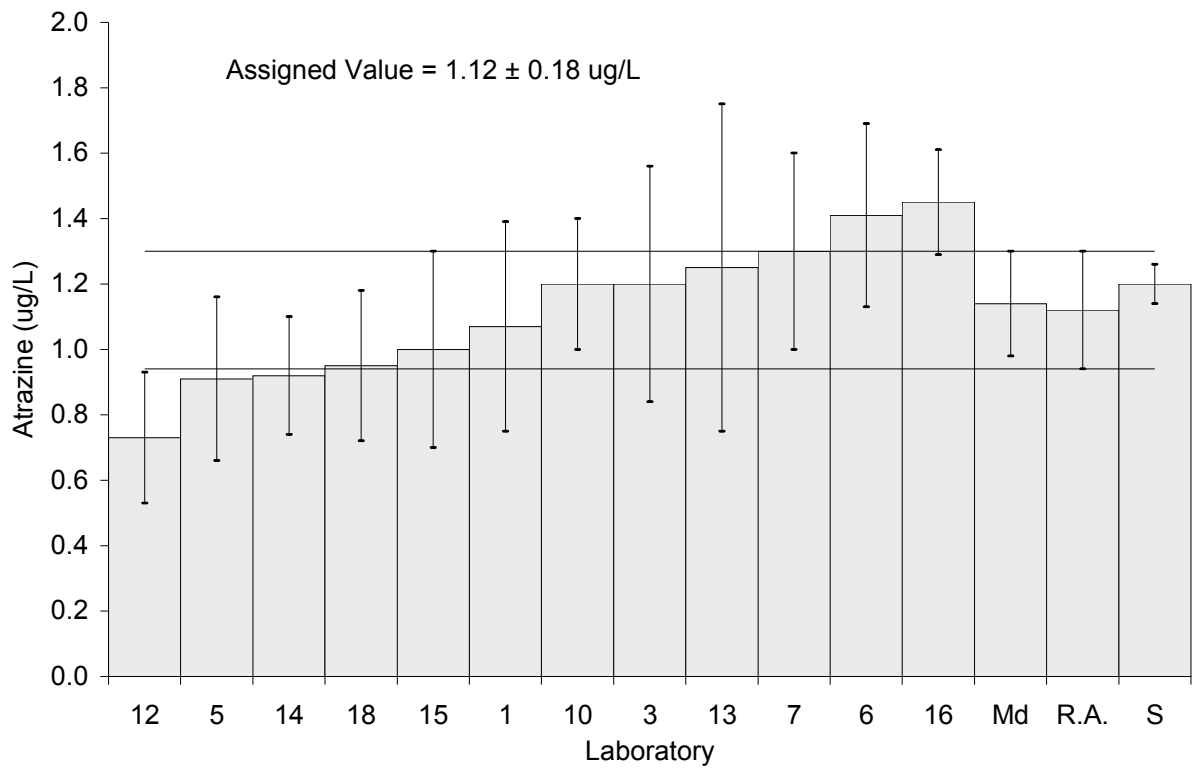
Trends in areas such as analytical performance, participation and reporting of uncertainty were identified. A greater acceptance and understanding of measurement uncertainty was evident.

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 organic pollutants in water are not necessarily compatible.

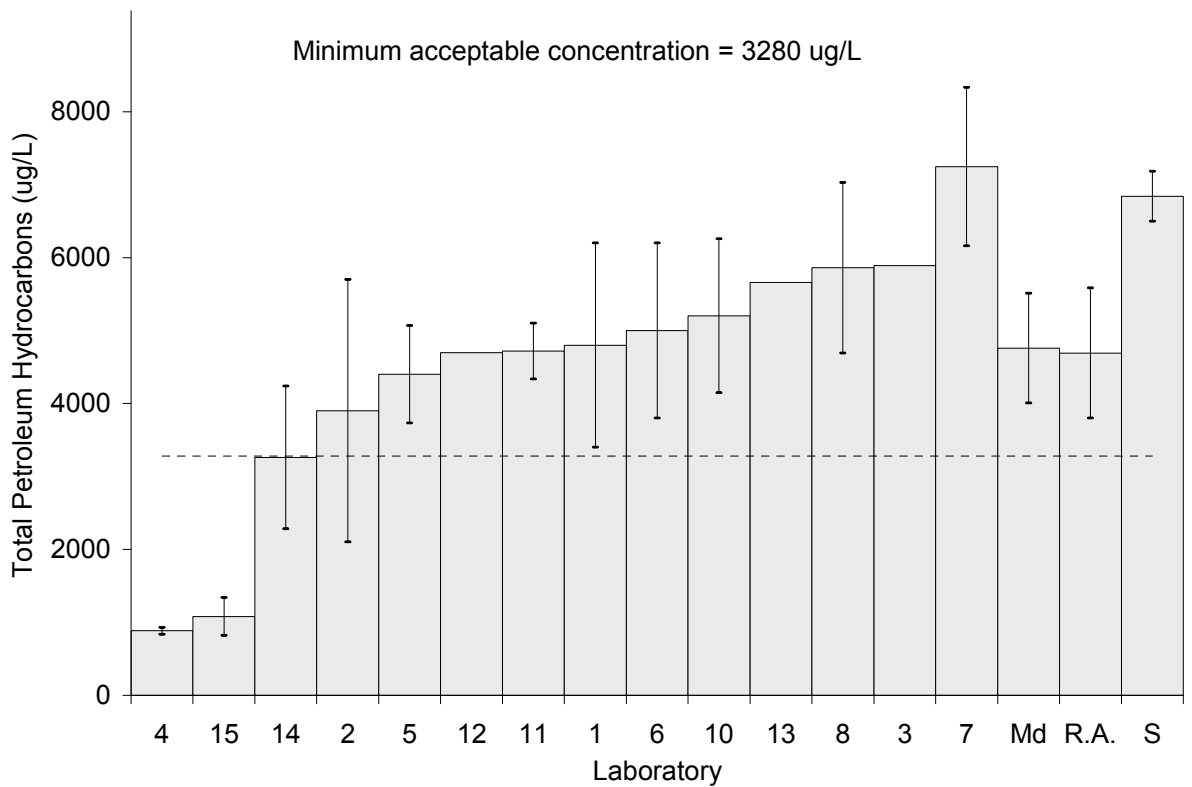
REFERENCES

ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing.



Md = Median, R.A = Robust Average, S = Spike.

Fig. 1. Interlaboratory results, fresh surface water spiked with atrazine.



Md = Median, R.A = Robust Average, S = Spike.

Fig. 2. Interlaboratory results, fresh water spiked with diesel fuel.

COMPARISON OF TWO SEQUENTIAL EXTRACTION PROCEDURES FOR THE FRACTIONATION OF ZINC IN AGRICULTURAL CALCAREOUS SOILS

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INTRODUCTION

Knowledge of the distribution of trace elements in soils and their availability to plants is important for maintaining and improving crop production and food quality (Wu et al., 2006). Zinc (Zn) plays an important role in plants, and deficiency in soils may markedly limit the production of cereals (Cakmak et al., 1999). More than 60% of arable soils in Iran are zinc deficient with an average yield depression of around 50%. The main causes of zinc deficiency in Iran are: calcareous soils with high pH values (mainly > 30% CaCO₃ with an actual range of 16-58% CaCO₃ with pH 7.9-8.5); high applications of phosphatic fertilisers; high concentrations of bicarbonate in irrigation water, and lack of Zn fertilizers (Ziaei and Malakouti, 2001). The distribution of metals among soil components is important for assessing the potential of soils to supply sufficient micronutrients for plant growth and retain toxic quantities of metals (Adriano, 2001). The quantification of chemical forms is normally based on the use of chemical reagents, often involving sequential extractions (Bermond, 2001; D'Amore et al., 2005).

METHODS

Samples from the surface horizons (0-20 cm) of 20 calcareous cultivated soils from Lorestan province, South-West Iran were used for the study. Soils were air dried then passed through a 2-mm sieve and retained for chemical characterisation assessment. Soil pH was measured potentiometrically in deionised water using a 1:2.5 (W:V) soil/water ratio. The equivalent CaCO₃ content was determined by the method presented by Allison and Moodie (1965). The potentially bioavailable fraction was estimated with a solution of 0.005 M DTPA, pH 7.3 as described elsewhere (Lindsay and Norvell, 1978). Different forms of zinc were sequentially extracted from the soils (1.0 g) with two sequential extraction procedures. The first one was a modification of the Tessier sequential extraction scheme proposed by Singh et al. (1988) (Procedure A) which is a seven-step method. The other one was the three-step modified BCR procedure as described by Rauret et al. (1999) (Procedure B). For total and residual Zn analysis, samples were digested in a 1:5 HClO₄:HF acid mixture for procedure A. For procedure B, the residual and total Zn contents in samples were estimated from aqua regia extractions following the procedure ISO 11466 (ISO, 1995b). All the soil samples were extracted and analyzed in duplicate by using each procedure.

RESULTS AND DISCUSSION

pH values of soils were up to 7.0 and characterized in general by a high calcium carbonate contents ranging from 5-49% (with the average of 32.14%). The small amounts of Zn were extracted with DTPA (0.02-1.01 mg kg⁻¹). To compare the results obtained by methods that have a different number of fractions (BCR, 4; Singh, 7), the fractions were arranged into four equivalent groups (acid-soluble (Ex+CAR), reducible (MnOX+AFeOX+CFeOX), oxidisable (ORG), and residual (RES)). To summarize, Table 1 gives the range values of the zinc fractions and total concentrations of Zn of soils extracted with two schemes. It is notable that the residual fraction extracted with both procedures was considerably higher than the others fractions for all soils. In the results obtained by using procedure A (As can be seen in Table 1) reducible fraction was the greatest among non-residual forms while oxidisable fraction was the greatest for procedure B. This could be explained by the fact that H₂O₂ can

simultaneously oxidize organic materials and soil sulfides. In procedure A, reducible fraction was extracted by the use of Oxalate/Oxalic acid buffered solution. One of the major disadvantages of this reagent is the formation of very stable complexes with aluminium and can lead to an overestimation of this fraction (Shuman, 1982).

Comparison of the results obtained by two sequential extraction procedures indicated that the amounts extracted for each fraction greatly varied depending on the methodology used.

Table1. range values of Zn fractions and total contents extracted in the soil samples by using Singh scheme (procedure A) and BCR scheme (procedure B)(mg kg⁻¹ dry weight) (n=20)

procedure	Solid phase zinc fractions				
	Acid soluble	Reducible	Oxidisable	Residual	Total
A	0.04-3.31	0.4-7.35	0.58-4.65	43.64-105.5	45.25-115.35
B	0.01-0.95	0-10.98	4.99-28.53	24.72-83.54	25.42-98.33

CONCLUSIONS

For the soils analyzed in this study zinc is dominantly associated with mineral lattice, while this fraction was greatest by the use of both procedures. Interpretation of results must not be based on the mineralogical fraction targeted but rather on the reagent used, implying a perfect knowledge of its action on the solid phase, therefore, the obtained values for Zn fractionations is dependent on the method used.

REFERENCES

- Allison L. E., and Moodie C. D. (1965) Carbonate. In: Black, C. A., et al., (Eds.), *Methods of Soil Analysis*. Agronomy no. 9, Part 2, 2nd ed. ASA, Madison, WI, USA, pp: 1379–1400.
- Bermond, A. (2001) Limits of sequential extraction procedures re-examined with emphasis on the role of H⁺ Ion reactivity. *Anal. Chim. Acta*. 445: 79-88..
- Cakmak, I., Kalayci, M., Ekiz, H., Braun, H. J., Kilinc, Y. and Yilmaz A. (1999) Zinc deficiency as a practical problem in plant and human nutrition in Turkey: ANATO-science for stability project. *Field Crops Res*. 60: 175-188.
- D'Amore, J. J., Al-Abed, S. R., Scheckel, K. G., and Ryan. J. A. (2005) Methods for speciation metals in soils: A review. *J. Environ. Qual*. 34: 1707-1745.
- ISO, 1995b. Soil quality. Extraction of trace elements soluble in aqua regia. ISO 11466: 1995(E).
- Lindsay W. L., and Norvell W. A. (1978) Development of a soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J*. 42: 421-428.
- Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, Ph. (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit*. 1: 57-61.
- Shuman L. M. (1982) Separating soil iron and manganese oxide fractions for micronutrient analysis. *Soil Sci. Am. J*. 46: 1099-1102.
- Singh J. P., Karwasra S. P. S., and Singh M. (1988) Distribution and forms of copper, iron, manganese and zinc in calcareous soils of India. *Soil Sci*. 146: 359-366.
- Wu, J., Norvell, W. A. and Welch, R. M. (2006) Kriging on highly skewed data for DTPA-extractable soil Zn with auxiliary information for pH and organic carbon. *Geoderma*. 134: 187-199.
- Ziaeiian A. H. and Malakouti M. J. (2001) Effects of Fe, Mn, Zn and Cu fertilization of wheat in the calcareous soils of Iran. In W. J. Horst et al. (eds) *Plant Nutrition – Food Security and sustainability of Agro-Ecosystems*, 840-841.

MDMA DEGRADATION IN SOIL

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INTRODUCTION

MDMA (3,4-Methylenedioxyamphetamine; Fig.1) popularly known as Ecstasy is a recreational drug with neurotoxic potential and is chemically and pharmacologically related to amphetamine (Mueller et al., 2007). MDMA is a ring substituted derivative of amphetamine and is a well established serotonergic neurotoxicant with significant abuse potential (Macedo et al., 2007). Since the early 1980s MDMA is the most commonly used rave drug (all-night dance parties known as ‘raves’) and is illicitly compounded in tablets, capsules, or powder (Oesterheld et al., 2004).

The illicit drugs are generally produced in small kitchen labs (commonly known as ‘clan lab’) using easily available precursor chemicals. The manufacturing process depends on the availability of the precursors and thus also produces a range of by-products. However, the clan lab wastes containing un-reacted precursor, residual target drug, and the by-products are illegally disposed off with the potential to contaminate different environmental matrices (e.g., soil, surface water, ground water, etc.). The potential impact of these clan lab chemicals is a growing concern among environmental scientists. The works so far have been reported mostly dealt with the presence of these compounds in surface and waste waters. There is a lack of systematic information on the fate of clan lab chemicals in soil. Thus, the present work was conducted to determine the fate of MDMA in soils of different physico-chemical properties.

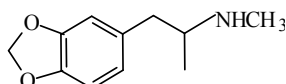


Fig. 1. Molecular structure of MDMA (3,4-Methylenedioxyamphetamine)

METHODS

Soil for the present study was collected from the Mawson Lakes campus of the University of South Australia (urban area), Sturt Gorge (native bush land) and Waite Campus (agricultural land) of The University of Adelaide, South Australia. The pH (in 1:2.5 H₂O) and organic carbon of the soils ranged between 5.64 (Waite Campus) to 8.91 (Mawson Lakes) and 1.11% (Mawson Lakes) to 2.88% (Sturt Gorge). The Mawson Lakes and Sturt Gorge soils were sandy loam while Waite Campus soil was loam in texture.

The degradation pattern of MDMA was determined at a spiking level of 100 µg g⁻¹ soil, 50% of maximum water holding capacity of soils, and at 25 ± 2^oC temperature both under the non-sterile and sterile conditions. The analytical technique (including soil extraction, sample clean-up, and analysis in HPLC-MS) was developed for precise quantification of MDMA from the test soils.

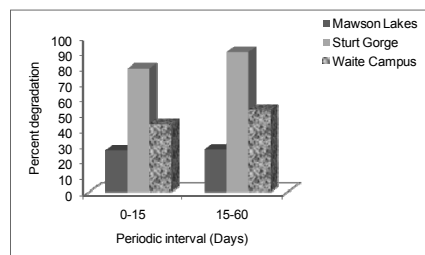
RESULTS AND DISCUSSIONS

In Fig. 2, the results of MDMA degradation in three test soils under non-sterile and sterile conditions have been presented. The result shows the percent degradation of MDMA in two time period: [1] between day 0 and 15 (Period 1) and [2] between day 15 and 60 (Period 2). In non-sterile soil condition, the percent degradation has increased from Period 1 to Period 2 for all three soils. On the other hand, the percent degradation under sterile condition for Mawson lakes and Waite campus soils showed almost a stable pattern between these two

time periods, while the Sturt Gorge soil recorded almost 50% decrease in percent degradation from Period 1 to Period 2.

The relative contribution of biotic and abiotic soil factors in MDMA degradation between day 15 and 60 is shown in Fig. 3. The result indicates a clear difference between the soils. The abiotic factors are significantly dominant over biotic factor for MDMA degradation in Mawson Lakes soil. In contrast, the contributions of biotic factor in comparison to abiotic factors are significantly higher for Sturt Gorge and Wait Campus soil.

[A] Non-sterile soil degradation



[B] Sterile soil degradation

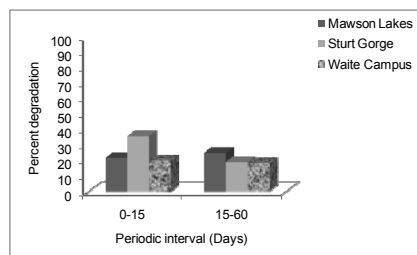


Fig. 2. Non-sterile (abiotic + biotic) and sterile (abiotic) soil degradation of MDMA

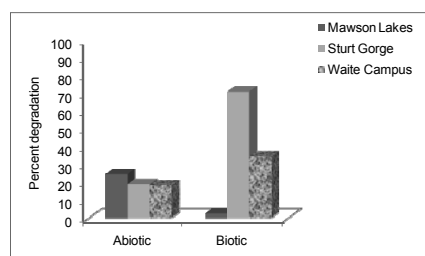


Fig. 3. Contribution of biotic and abiotic soil factors in MDMA degradation between 15 to 60 days

CONCLUSION

The results of the present study clearly indicated that the degradation of MDMA depend largely on the role of biotic and abiotic soil properties.

ACKNOWLEDGMENT

This work was supported by a National Drug Law Enforcement Research Fund grant.

REFERENCES

- Macedo, C., Branco, P.S., Ferreira, L.M., Lobo, A.M., Capela, J.P., Fernandes, E., Bastos, M.L. and Carvalho, F. (2007) Synthesis and cyclic voltametry studies of 3,4-Methylenedioxyamphetamine (MDMA) human metabolites. *J. Health Sci.* 53: 31-42.
- Mueller, M., Peters, F.T., Ricaurte, G.A. and Maurer, H.H. (2007) Validated liquid chromatographic-electrospray ionization mass spectrometric assay for simultaneous determination of 3,4-methylenedioxyamphetamine and its metabolites 3,4-methylenedioxyamphetamine, 3,4-dihydroxyamphetamine, and 4-hydroxy-3-methoxyamphetamine in squirrel monkey plasma. *J. Chromatogr B.* 855: 262-270.
- Oesterheld, J.R., Armstrong, S.C. and Cozza, K.L. (2004). Ecstasy: pharmacodynamic and pharmacokinetic interactions. *Psychosomatics* 45: 84-87.

ZERO-VALENT IRON TREATABILITY STUDY USING TRICHLOROETHYLENE SPIKED DEIONISED WATER YIELDS RATE CONSTANT CONSIDERABLY LOWER THAN THAT FOR A HIGHLY SALINE CONTAMINATED GROUNDWATER

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INTRODUCTION

Zero valent iron (ZVI) based permeable reactive barrier (PRB) is commonly being used to remediate groundwater (GW) across the world (Gavaskar et al. 2000). Along with chlorinated hydrocarbons, ZVI also removes arsenic and other heavy metals. Because of its low operational cost, PRBs are a very popular technology in the remediation sector (Gavaskar et al. 2000). In most of the PRB installation sites, β -elimination is the major pathway via chlorinated hydrocarbon demineralisation. Similar to other material used for PRB, the performance of the ZVI PRB depends to a large extent on both the contaminants of concern and the GW parameters. At a historically long-term contaminated site in Australia, GW was found to be contaminated with trichloroethylene (TCE) and Cr(VI). GW is slightly alkaline in pH with high concentration of calcium (25 mg/L), total inorganic carbon (140 mg/L) and chloride (830 mg/L). These parameters are significantly different from that reported in the literature (Gavaskar et al. 2000) for sites where PRBs have been installed. The rate constant is vital for determining the thickness of reactive barrier. Batch study is an economical and rapid method for determining the TCE degradation rate (Golpagar et al. 1997). Commonly, batch study is conducted using freshly spiked deionised (DI) water to determine the rate constant for varying dosage of ZVI. Column studies using spiked water are also used to understand the failure mode of the PRB under dynamic condition (Gillham and O'Hannesin 1994) using freshly spiked DI water. However, the composition of GW is considerably different from DI water and this may impact on the TCE degradation rate constant. In this study we investigate the potential difference in TCE degradation when treatability studies are conducted using spiked DI water as opposed to real field contaminated ground water.

METHODS

The required amount of TCE stock solution prepared in methanol was added to DI and GW to maintain final solution concentration 5 mg/L of TCE. TCE spiked water was slowly transferred into a 40 mL vial containing ZVI until it overflowed. Then each vial was capped with Teflon lid. These vials were equilibrated on the Ratek® platform shaker at 125 RPM continuously at 18 °C room temperature. Samples were taken at 0, 6, 12, 24, 48, 72, 96 and 120 hours. At each sampling procedure, one reference sample and 3 other samples were taken. By using 10 mL syringe, the samples were transferred into the 20 mL head space vials and sealed using Teflon septa covered with aluminum. This experiment was performed using TCE spiked GW and DI water. Experiments were performed with 20 g, 14 g, 10 g, 7 g, 5 g and 3.5 g ZVI dosage in 40 mL vials.

The sample was analysed in the Agilent GC- μ ECD instrument with headspace sampler. 30 m length, 0.25 mm internal diameter and 1.40 μ m film thickness and DB 624 column was used. The set initial and final temperature of the column were 35 °C and 200 °C respectively with temperature rise rate of 10 °C /min for 14 min and then 50 °C/min for 18 min. Inductive coupled plasma mass spectrometry (ICP-MS) was used to measure the heavy metal(loid)s in

the GW using EPA method 6020a. Chloride was analyzed by using Ion chromatography (DIONEX ICS-2000) with an AS18 column at 35 °C.

RESULTS AND DISCUSSION

The TCE reduction rate was slow up to 24 hours of treatment in both spiked DI water and GW. From 24 to 96 hours TCE degradation as well as *cis*- dichloroethylene (c-DCE) formation were linear. After 96 hours c-DCE too reduces. It is likely that TCE is being removed due to adsorption on to the ZVI surface for up to 24 hours following which it is removed due to the electron production from ZVI corrosion. *Trans*- dichloroethylene (t-DCE) was not detected.

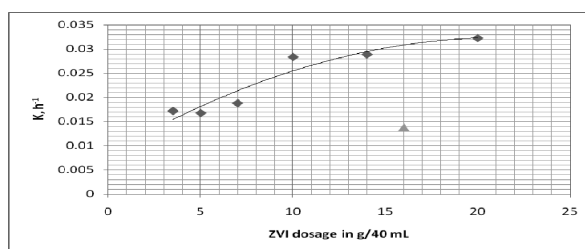


Fig 1. The plot of rate constant k variation with ZVI dosage in 40 mL batch treatment of 5 mg/L TCE spiked GW and DI water. GW ♦ ,DI water ▲

Fig 1 shows that rate constant variation with ZVI dosage for TCE spiked GW as well as DI water. K value increases with ZVI dosage for ZVI treated GW. The K value for TCE spiked DI water is lower than that of GW. This is mainly due to the presence of higher chloride in GW which causes pitting corrosion in spite of the fact that it has higher possibility of passivating ZVI surface by CaCO₃ precipitate.

Chloride destabilises the passive film on the iron surface and this can induce corrosion pit formation (Lu et al. 2006).



Eqn. (1) shows the possibility of formation of Cl₂ which is a highly oxidizing agent and can promote corrosion. This may be the reason for the higher K value in the GW sample compared to the DI water sample. The effect of chloride may have been slightly compensated for by precipitation of carbonate at the ZVI: water interface in the GW samples. This could be a possible explanation for the low k values in the GW treatment. The half life range for GW was 21.5 to 40 hrs whereas for TCE spiked DI water 50 hours. These results demonstrate that treatability studies conducted using TCE spiked DI water could lead to construction of PRB's with thickness much greater than needed to effectively degrade TCE. This has significant implication to the cost of such barriers.

CONCLUSION

Our current study demonstrates that rate constant obtained using freshly spiked DI water (0.0125 h⁻¹) is significantly lower than that obtained using contaminated GW (0.03 h⁻¹). It is also evident from this study that treatability studies conducted using freshly spiked DI water can lead to PRB's with thickness much greater than needed to effectively degrade TCE.

REFERENCES

- Gavaskar, A., Gupta, N., Sass, B., Janosy, R. and Hicks, J. (2000) Design guidance for application of permeable reactive barriers for groundwater remediation. *SERDP*.240p
- Golpagar, J., Grulke, E., Tsang, T. and Bhattacharyya, D. (1997) Reductive dehalogenation of trichloroethylene using zero-valent iron. *Environmental progress* 16:137-143.
- Gillham, R.W. and O'Hannesin, S.F. (1994) Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground water*. 32 : 958-967.
- Lu, M.C., Anotai, J., Chyan, J.M. and Ting, W.P. (2006) Effect of chloride ions on the dechlorination of hexachlorobenzene in the presence of zero-valent iron. *Practice periodical of hazardous, toxic, and radioactive waste managements*. 226-230.

PHOTOCATALYSIS FOR EFFICIENT TREATMENT OF FLAME RETARDANTS (PBDES) BY NANO-SIZED TiO₂

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INTRODUCTION

Since the 1970s, the demand of brominated flame retardants has been increasing (Wang et al., 2007). The annual global production of polybrominated diphenyl ethers (PBDEs) increased from 40,000 tonnes (Arias, 1992), to around 67,000 tonnes between 1992 to 2001 (BSEF, 2006). They are generally used in polymer and textile products as additive flame retardants (de Wit, 2002; Rahman et al., 2001). PBDEs added resins or polymers are also common components of electrical appliances, contributing to the release of PBDEs from electronic waste (e-waste) (WHO, 1994). The majority of deca-BDE from Asia is produced in eastern China (Wang et al., 2007) and the release of PBDEs into the environment can be attributed to the synthesis process, inappropriate disposal, incorporation into products, and from hazardous waste sites (Danish Environmental Protection Agency, 1999). Technology is advancing at such a rapid pace in the past decade that the life-span of electronic appliances are becoming shorter and shorter, many developed countries export e-waste to developing countries in East and Southeast Asia for recycling. Illegal and inappropriate dumping and recycling of e-waste are believed to be two major sources of PBDEs contamination in the environment (Wang et al., 2005). In order to cope with an uprising application of PBDEs and its release into the environment, advanced remediation technologies should be developed. Advanced oxidation processes (AOP) is one possible method for removing trace levels of emerging chemicals (e.g. acetaminophen, antipyrine, atrazine, caffeine and progesterone) in wastewater (Klamerth et al., 2009).

METHODS

Nano-scaled titanium (IV) oxide (< 100 nm) was applied to evaluate its capability in the degradation of BDE-209 in 0.1 % DMSO under visible light. The photocatalytic degradation of BDE-209 was studied in different time intervals (4 h, and 1, 2, 3, 4, 5, 6 and 14 days), pHs (pH 4, 6, 7, 8, 12), humic acids concentrations (5, 10, 20 and 40 mg/L) and crystalline forms of TiO₂ (anatase, rutile, and mixture of anatase and rutile). Hydroxyl radical which is a kind of reactive oxygen species produced during photocatalytic degradation was measured by using a fluorescent dye, dichlorofluorescein diacetate (H₂DCF-DA). The radicals produced in different operation conditions were then quantified by a microplate reader (λ excitation = 498 nm; λ emission = 522 nm) (Foucaud et al., 2007). The residual PBDE congeners after photocatalytic degradation of BDE-209 by TiO₂ were also analysed by gas chromatography-mass spectrometry (GC-MS) according to US EPA standard method 1614 (US EPA, 2007).

RESULTS AND DISCUSSION

The photocatalytic degradation of BDE-209 in the current study actually followed the first-order rate law in the beginning 6 days ($y = 1.88 - 0.0945(t)$; where y is the log concentration of BDE-209 and t is reaction time in terms of days). According to the equation, the half-life for BDE-209 degradation in this study was 3.05 days. It was found that the degradability of TiO₂ was attributed to its photocatalytic activity but not the small size of the particles, even

though the nano-size might increase the effective reaction areas. The hydroxyl radicals produced by TiO₂ increased from 4 to 8 h and then decreased until Day 6. Although there was a drop after 8 h, the levels of hydroxyl radicals still remained at double of the control level. In general, the majority of photocatalytical degradation products after treatment with nano-sized TiO₂ under three different operational conditions were dominated by penta- and tetra-BDEs (ranged from 25.7 % to 40.6 %). The photocatalytical degradation of BDE-209 performed the best at pH 12 (93 % ± 1 %), 10-20 mg/L (91.6 % ± 3.21 %; 91.9 % ± 0.952 %) of humic acid and in the form of anatase/rutile TiO₂ (82 % ± 3 %). There was a significant positive correlation between ROS induction and BDE-47 ($r = 0.652$, $p < 0.01$) and BDE-99 ($r = 0.835$, $p < 0.01$) production at pH 12. There was also a significant correlation between ROS induction and production of BDE-47 ($r = 0.703$, $p < 0.01$) and BDE-99 ($r = 0.696$, $p < 0.01$) in 20mg/L of humic acids. On the other hand, a significant negative correlation ($r = -0.696$, $p < 0.05$) obtained between ROS induction and concentration of BDE-209 in the anatase/rutile mixture, suggesting that the increase of ROS might be related to BDE-209 degradation.

CONCLUSIONS

There is an urgent need to promote the removal efficiency of PBDEs owing to its rapid production and application in industry. TiO₂, a promising photocatalyst used in AOP was applied for the removal of BDE-209. The results showed that TiO₂ can promote the degradation of BDE-209, with a shorter half-life than natural degradation. The degradability of TiO₂ was attributed to its photocatalytic activity but not the small size of the particles. The photocatalytical degradation of BDE-209 performed the best at pH 12, 5-20 mg/L of humic acid and in the forms of anatase/rutile TiO₂. The findings provide crucial information for the advanced treatment of PBDEs and may also improve the advanced oxidation process in wastewater treatment facilities before applying further treatment. Hence, the removal efficiency of PBDEs can be enhanced and operation cost may be reduced.

REFERENCES

- Arias, P. (1992) Brominated diphenyloxides as flame retardants: bromine based chemicals. Consultant report to the Organisation for Economic Co-operation and Development, Paris.
- Bromine Science and Environmental Forum Total Market Demand. (2006) Available at www.bsef.com.
- Danish Environmental Protection Agency. (1999) Brominated flame retardants: substance flow analysis and assessment of alternatives. Environmental project Nr. 494.
- de Wit, CA. (2002) An overview of brominated flame retardants in the environment. *Chemosphere* 46:583-624.
- Foucaud, L., Wilson, M.R., Browna, D.M., Stone, V. (2007) Measurement of reactive species production by nanoparticles prepared in biologically relevant media. *Toxicol. Lett.* 174:1-9.
- Klamerth, N., Miranda, N., Malato, S., Agüera, A., Ferna'ndez-Alba, A.R., Maldonado, M.I., Coronado, J.M. (2009) Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO₂. *Catalys. Today* 144:124-130.
- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N. (2001) Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. of The Total Environ.* 275:1-17.
- Wang, D.L., Cai, Z.W., Jiang, G.B., Leung, A., Wong, M.H., Wong, W.K. (2005) Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. *Chemosphere* 60:810-816.
- Wang, Y., Jiang, G., Lam, P.K.S., Li, A. (2007) Polybrominated diphenyl ether in the East Asian environment: A critical review. *Environ. Int.* 33: 963-973.
- World Health Organisation (WHO) (1994) Brominated diphenyl ethers. *Environ Health Crit* 62.

EFFECT OF OIL SPILLAGE ON THE PROPERTIES OF SOIL AND ENVIRONMENT AROUND THE MARKETING OUTLETS OF SOME PETROLEUM MARKETING COMPANIES IN CALABAR CROSS RIVER STATE, NIGERIA

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INTRODUCTION

Fossil fuel appeared to offer limitless source of energy to drive development. While oil and energy provides multiple benefits to human society, every stage of its life cycle from exploration to use can have harmful effects on the environment, the soil physicochemical and biological properties and human health due to its spillage (Aghalino, 2000). This negative impact of oil spillage includes destruction of life, loss of fertile soil, pollution and damage to the ecosystem of the host communities (Abi and Nwosu, 2009). This work was conducted to investigate the effects of oil spillage on the physical, chemical and biological properties of soil and vegetation around petrol-filling stations in Calabar metropolis.

METHODS

Soil samples were collected from the surroundings of five petroleum marketing companies in Calabar, Nigeria (i.e. Mobil, Total, Conoil, Nigerian National Petroleum Company (NNPC) mega station, and Oando petrol-filling stations). The samples were collected from the oil spilled affected soils and non-oil affected soils to serve as control. Composite soil samples were collected from the topsoil surface (0 - 15 cm) using soil auger. Some physico-chemical properties that reflect soil nutrients content and fertility status (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , C, N, P, pH, ECEC, particle size analysis, electrical conductivity, and hydrocarbon content) and microbial flora populations were determined using standard physico-chemical and biological methods.

RESULTS AND DISCUSSION

Results from the oil affected and non-oil spilled affected soils were compared. There was a significant decrease in Ca^{2+} , Mg^{2+} , K^+ , ECEC, silt fraction, clay fraction in oil affected soils as well as significant increase in the sand fraction content, Na^+ content, electrical conductivity, hydrocarbon content of the oil-spilled affected soils when compared with the non-oil spilled affected soils. The acidic nature of the soils could not be attributed entirely to the oil-spilled since the non-oil affected soils were equally acidic. The results of microbial flora of areas with and without oil spilled show little effect on the microbial populations of the soils studied. The average microbial population of the soils with oil-spilled was 2.78×10^6 Cfug, while that without oil-spilled was 3.6×10^6 Cfug for bacteria count. The fungi populations of oil affected soils was 3.4×10^4 Cfug while the non-oil affected soils was 3.0×10^4 Cfug. The microbes identified from oil affected soils for both bacteria and fungi are different from the ones identified from non-oil affected soils.

Table 1. Chemical properties of the soil under study at Calabar, Nigeria

Sample	pH	Org. C. (%)	Avail P. (mg/kg)	Total N (%)	EC (Ms cm ⁻¹)	THC (ppm)
Total-A	5.8	3.59	75.12	0.31	44.0	719
Total-B	6.2	1.50	80.75	0.12	40.0	281
NNPC-A	5.2	2.65	82.50	0.22	75.0	366
NNPC-B	5.5	2.05	82.75	0.17	57.0	112
Oando-A	5.5	1.60	88.75	0.13	34.0	770
Oando-B	5.8	2.39	85.50	0.20	27.0	295
Conoil-A	5.6	1.08	74.63	0.09	73.0	808
Conoil-B	6.0	3.59	90.13	0.30	41.0	289
Mobil-A	5.7	3.93	82.13	0.33	99.0	816
Mobil- B	5.9	3.13	79.38	0.26	66.0	290

Keys: Sample-A was taken at the main oil-affected area; Sample-B was the non-oil affected area. Org C.= Organic carbon, Avail P.= Available Phosphorus (Bray-1); Total N= total nitrogen, EC = electrical conductivity; THC = Total Hydrocarbon Content

CONCLUSION

The significant variation of the results of physicochemical and microbiological population observed, are indicative of the effect of oil spillage on the soils. The effects of oil-spillage on the environment around the petroleum filling stations was also observed by the scanty and burnt nature of the vegetation around the stations. There were some health hazard effects on the people that are constantly around the filling stations assessed due to exposure to petroleum products.

Keywords

Petroleum Products Marketing Outlets, Oil Spilled soil, Non-oil spilled soil, Physico-chemical, Biological Properties

REFERENCES

- Abi, T. A. and Nwosu, P. C. (2009). The effects of oil spillage on the soil. *Academic Journals International* 2009, Vol. 9: 78-87.
- Aghalino, S. O. (2000). Petroleum exploration and the agitation for compensation by Oil mineral producing communities in Nigeria. *Journal of Environmental Policy* issue Vol. 1: 11

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REMEDIATION OF FORMER STEELWORKS, ALEXANDRIA NSW

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INTRODUCTION

Enviropacific Services were engaged in 2009 to undertake remediation of a former steelworks in Alexandria, NSW. Site investigations revealed a range of contaminants impacting the local Botany sands aquifer, including TPH, PAHs, asbestos and Heavy Metals. The local groundwater was also heavily impacted by heavy metals, PAHs and TPH, including phase separated hydrocarbon in some areas. The aim of the project was to remediate the impacted soil and groundwater at the site to achieve sign off from the site auditor without significant ongoing constraints being applied to future development. Additionally, the works needed to provide an effective long-term groundwater flow barrier between the site and adjacent sites to ensure that following remediation the site would not be re-contaminated.

Due to the wide range of contamination issues and large scale of impact, the proposed remediation strategy was highly complex, involving design and construction of a 12 m deep, 300 m long groundwater cut-off wall, design and construction of a groundwater dewatering and treatment system to treat approximately 1 ML/day of highly impacted groundwater to meet stormwater discharge criteria, design and construction of a soil treatment structure with extensive negative air pressure carbon filtration system, and treatment and/or disposal of approximately 27,000 tonnes of contaminated soil.

METHODS

Design and Construction of Groundwater Cut-off Wall

The design and construction phase for the groundwater cut-off wall included a number of specific challenges to Enviropacific, including deep and substantial obstructions within the wall alignment, construction adjacent to already dilapidated structures, and managing the impact of the contaminants on the grout curing process. In response to these challenges Enviropacific employed a range of methodologies, including grouting with a fly ash/cement blend to overcome curing issues, design of a fully cantilevered cut-off wall to remove the need for intrusive anchoring works beneath neighbouring properties, soil-mix pile wall construction to minimise local ground disturbance and minimise spoil production, and realignment of the wall in some areas to avoid impacting protruding adjacent footings and buried structures. In situ micro-fine grout stabilisation techniques were employed to stabilise the hydrocarbon contamination where the dilapidated nature of the surrounding building prevented pile wall construction and excavation.

Dewatering and Groundwater Treatment

Excavation and dewatering sequences were designed to be undertaken in a staged manner to accommodate the high groundwater recharge rates of the Botany Sands Aquifer. The limiting factor for the dewatering and treatment system was the maximum flow rate of the water treatment plant, approximately 20L/s. Excavation of the high level waste was undertaken below the groundwater table prior to dewatering to minimise accidental spread of the contamination into underlying less impacted soil layers. Dewatering was undertaken using a series of spearpoints manifolded to a 6 inch diesel pump. Extracted water was subsequently pumped through the integrated water treatment system, which included sedimentation, flocculation, coagulation, pH adjustment, zeolite filtration and granulated activated carbon (GAC) filtration.

Soil treatment

A purpose built 1000 m² soil treatment structure with vapour extraction system was constructed to minimise impacts on local residents during treatment of the highly odourous contaminated soil. The targeted soil treatment strategy included bioremediation, landfarming and large scale chemical oxidation to reduce concentrations of particularly recalcitrant hydrocarbons to required levels.

RESULTS AND DISCUSSION

Design and Construction of Groundwater Cut-off Wall

Early consideration of potential construction issues during the design phase for the cut-off wall ensured only minor design adjustments were required during construction to achieve the required outcome. In spite of the inclusion of fly-ash within the grout mix, curing periods for the wall ranged broadly, with sections requiring between 4-35 days of curing to achieve the minimum MPa. The slow curing sections were found to generally coincide with the location of peat layers, and high hydrocarbon concentrations within the soil profile. No visible leaks could be observed in the wall during deep excavation works, a testament to the effectiveness of the wall in restricting groundwater flows.

Water Treatment Results

Hydrocarbon contaminants, along with the majority of heavy metals within impacted groundwater were readily removed by the treatment plant, with extracted groundwater consistently returning non-detects following treatment. However, Aluminium concentrations continued to remain above the approved discharge criteria during preliminary treatability trials. The Aluminium exceedences were subsequently addressed by applying a combination of increased lime, flocculant and coagulant dosing, along with increasing the initial sedimentation period using contingency storage tanks. Subsequent testing revealed a maximum 95% removal efficiency for Aluminium during the ongoing groundwater treatment works. In spite of the high removal efficiency being achieved, Aluminium concentrations remained above the ANZECC guideline criteria. In response, and in conjunction with regulatory authorities and the site environmental consultant a more suitable risk based approach was developed to address the high aluminium concentrations.

Treatment of Contaminated Soil

During the project >11,000 tonnes of hydrocarbon impacted waste underwent treatment inside the structure, with around 5000 tonnes being treated to below site criteria, and reused on-site. TPH concentrations were reduced from between 3,000-10,000 mg/kg to below the site criteria of 1,000 mg/kg. Ex-situ chemical oxidation provided limited success in reducing TPH concentrations, with reductions being in the order of 100-200 mg/kg for TPH¹⁰⁻³⁶.

CONCLUSIONS

The desired remediation outcomes were achieved and the car park reinstated at the completion of the works. The design and construction of the groundwater cut-off wall was highly successful, producing no visible seepages or leaks at the completion of construction, thereby providing increased confidence of the wall preventing re-contamination of the remediated site by transport from adjacent properties. Significant savings were made in reducing offsite disposal costs of soil and water through effective and integrated treatment methods.

PHYTOAVAILABILITY OF BARIUM IN SOILS CONTAMINATED BY BARITE

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INTRODUCTION

Barium (Ba) is a Group 2 element that shares several chemical characteristics with calcium (Ca). Barium, however, is not an essential nutrient to animals and plants but instead is known to cause several deleterious effects on most organisms. Barite (BaSO_4) is a highly insoluble mineral. It is insoluble in water, acid and bases, and on its own is unlikely to cause a risk to humans or the environment. Ba may be highly mobile in soil as Ba primarily associates with soil colloids by ion exchange. However, barite solubility is extremely important in the environment (Hatipoglu et al., 1990, Lasley et al., 2010, NTP, 1994). The aim of this paper is to examine the phytoavailability of Ba from barite contaminated soils from an urban area.

MATERIALS AND METHODS

Six soil samples contaminated with barite plus a control were sampled in duplicate. Samples were sieved through 2-mm sieves for general soil characterisation and plant growth studies. Barium concentrations were measured using both microwave-assisted acid digestion and X-ray Fluorescence (XRF) methodologies. Mineralogy of the samples was determined in samples L7 and L10 (control) using X-ray Diffraction (XRD). All mineralogy and "total" concentration determinations were performed by commercial laboratories.

Lettuce (*Lactuca sativa* L. 'Great Lakes') seeds were sown to plant pots containing barite contaminated soils. Each pot was lined with fine nylon mesh and 200g of air-dry soil added. Each pot was placed within a collecting tray, to which reverse-osmosis water was added ($13 \mu\text{S cm}^{-1}$). Sufficient seed was added to ensure germination, which was trimmed to 1 plant per pot. Each soil sample (including duplicate samples) was replicated 4 times. To sample pore-water from the pots, soils were re-moistened 14 days prior to sampling, allowing for wet-dry cycles. Five days prior to sampling, soils were brought to field capacity, allowed to drain for another two days, prior to rewetting to field capacity. Twenty-four hours later, soil solution was extracted with RhizonTM samplers. Soils were again allowed to drain for five days, before re-wetting to field capacity, allowing 24 h and re-sampling soil solution. All soil samples were analysed using inductively coupled plasma- mass spectroscopy (ICP-MS) (Agilent 7500c) after appropriate dilutions. Quality control was monitored during analysis by addition of 50 $\mu\text{g/L}$ check samples and blanks every 20 samples. Recovery of check samples was always between 90-110%. Ba content in plant tissue was conducted by digesting the oven dried samples in 5 ml of concentrated nitric acid.

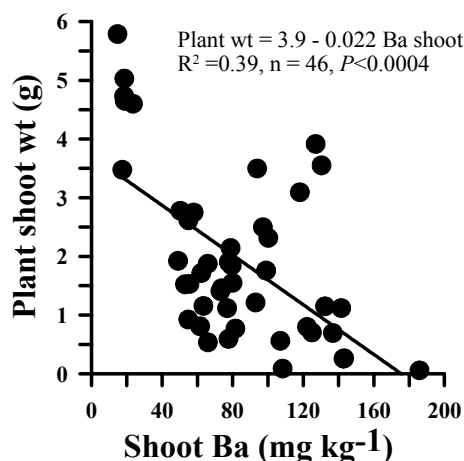


Figure 1. Relationship between dry weight shoot production and Ba accumulation in plant shoots.

RESULTS

Barium concentrations estimated from acid digestion and XRF showed extremely high Ba concentrations (up to 29.2% Ba). Barium concentrations differed dramatically between the two total concentrations estimates. Acid digestion results are in all cases far below that determined by XRF. Although “total” concentrations estimates based on acid digestion methods are useful, differences in the two measures increased as the XRF concentration increased. The total Ba in controls using XRF was 500-700 mg kg⁻¹. Concentrations in contaminated soils determined by XRF were in the range of 0.13% to 29.2%. Samples with the highest Ba concentrations had 45% BaSO₄.

Lettuce dry weight biomass in barite enriched soils was significantly reduced compared to the control soils. Moreover, all soils enriched with Ba supported significantly lower lettuce growth than the control ($P < 0.05$). Growth reductions relative to control soil were greatest in soils L9 and L4, where almost complete growth retardation was observed. In soils where plant growth was severely impacted leaves become yellow, indicating general chlorosis in leaves. Dry weights were did not correlate with either XRF or acid extractable metal concentrations. Ba concentrations measured in shoots was linearly related to the reduction in dry matter production (Figure 1) and measured porewater concentrations. Dry matter production was not related to soil pH, organic C content, organic N content or other soil properties. The results show that despite BaSO₄ being highly insoluble in aqueous solutions and acid, Ba in BaSO₄ enriched soil may be phytoavailable in some soils.

CONCLUSION

The results show that despite barite being a highly insoluble mineral in water and acid, barite contamination resulted substantial growth reductions in *L. sativa*. Barium in shoot tissues was related to dry matter production, and not other parameters, indicating Ba from BaSO₄ is a potential problem in soil despite earlier indications in the literature.

REFERENCES

- HATIPOGLU, S., EYLEM, C., GOKTURK, H. & ERTEN, H. N. 1990. Sorption of strontium and barium on clays and soil fractions. *Sciences Geologiques - Memoire*, 86, 79-86.
- LASLEY, K. K., EVANYLO, G. K., KOSTYANOVSKY, K. I., SHANG, C., EICK, M. & DANIELS, W. L. 2010. Chemistry and transport of metals from entrenched biosolids at a reclaimed mineral sands mining site. *Journal of Environmental Quality*, 39, 1467-1477.
- NTP 1994. NTP technical report on the toxicology and carcinogenesis of barium chloride dihydrate (CAS no. 10326-27-9) in f344/N rats and B6c6F1 mice (drinking water studies),. National Toxicology Program.

FRACTIONATION CHANGES OF CADMIUM WITH TIME IN SOILS TREATED WITH CADMIUM CHLORIDE IN DIFFERENT MOISTURE REGIMES

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INTRODUCTION

Chemical forms of heavy metals change over time and it is often metal mobility and bioavailability reduces with over time (Lim et al., 2002 and Ma and Uren, 1998). Metals in soils may be differentiated into soluble+ exchangeable, carbonate-, organic matter-, Mn oxide-, amorphous Fe oxide-, crystalline Fe oxide-bound and residual fractions (Singh et al., 1988). Generally, metals associated with soluble+ exchangeable fractions are considered readily mobile and easily bioavailable, while residual form is considered to incorporate into crystalline lattice of soil minerals and appear to be the most inactive. The carbonate-, Fe-Mn oxide- and organic matter- bound fractions may be considered relatively active depending on the actual physical and chemical properties of soil (Lu et al., 2005). Han and Banin (1997; 1999) investigated that highly soluble forms are converted into less soluble ones over time. Kandpal et al. (2004) reported that the transformation of Cd depends on the soil moisture regime and soil characteristics. Understanding the factors affecting Cd fractionation in soils and alteration between these fractions is important in understanding its mobility and bioavailability in the environment.

METHODS

Three surface (0-10 cm) soil samples of acidic, alkaline and neutral soils were collected from different locations. Properties of these soils are presented in Table 1. Cadmium chloride was added to each treatment to achieve a final Cd concentration of 50mg/kg⁻¹ soil. The treated soils were incubated at field capacity or continuous flooding at room temperature. At the end of 1, 2, 4, 8 and 16 weeks of incubation, each treatment was selected for sequential extraction by scheme of Singh et al. (1988). The total metal concentrations in soils were determined after digestion with HF-HClO₄. The data were analyzed using variance analysis based upon a three factorial completely randomized design with three replications. The statistical significance was tested at probability level of P = 0.05.

Table 1. General properties of soil samples used in the study

General properties	Acidic soil	Alkaline soil	Neutral soil
pH (1:2.5 _{water})	5.8	8	7.1
O.M. (%)	0.59	2.46	5.41
Texture	Clay Loam	Clay	Silty Clay
C.E.C. (c mol kg ⁻¹)	10.22	13.7	18.59
EC (dS m ⁻¹)	1.2	2.5	1.4
% CaCO ₃	0.34	33	1.3
Field capacity (%)	21.52	28.86	32.66
Total Cd (mg kg ⁻¹)	2.23	3	2.4

RESULTS AND DISCUSSION

The water soluble and exchangeable fraction of Cd was found to be the highest in acidic soil followed by neutral and alkaline soils. Lower soil pH in the acidic soil increased the availability and mobility of the metal ions in the soil solution. In general, soluble+exchangeable Cd decreased at the end of the incubation period indicating that a decreased availability of Cd occurred after long term incubation. The carbonate bound Cd was highest in the alkaline soil that had the highest CaCO₃ content. Co-precipitation of heavy metals on carbonates and sulfides could be important under continuous flooding. Carbonate bound Cd in alkaline and neutral soils decreased and in acidic soil increased at the end of incubation period. Organic matter bound Cd was highest in the neutral soil followed by the alkaline and then the acidic soils. At the end of the incubation period, the content of organically bound Cd registered an increase in alkaline and acidic soils and decrease in neutral soil. Mn oxide bound Cd was highest in the acidic soil followed by the neutral and then the alkaline soils. The Cd bound to amorphous iron oxide (AF₂O₃) of alkaline soil was highest than two other soils. This fraction registered an increase in alkaline and neutral soils at the end of 16 weeks. There was no different between two moisture regimes in all soil over time. Cd bound to crystalline iron oxide (CF₂O₃) was highest in acidic soil. This form at the end of incubation time increased in neural soil and decreased in alkaline soil. The residual fraction of Cd was also the highest in acidic soil followed by the alkaline and then the neutral soils. Field capacity moisture regime resulted in a higher content of residual. This fraction was found to increase at the end of 16 weeks in alkaline and neutral soils but decreased in acidic soil.

CONCLUSIONS

Carbonate fraction is dominating form in most soils. Soluble forms of Cd change into less soluble forms with over time. There are slightly different between the both moisture regimes in distribution of Cd.

REFERENCES

- Han, F.X., Banin, A. (1997) Long-term transformation and redistribution of potentially toxic heavy metals in arid zone soils: I. Under saturated conditions. *Water Air Soil Pollut.* 95: 399-423.
- Han, F.X., Banin A. (1999) Long-term transformation and redistribution of potentially toxic heavy metals in arid zone soils: II. Incubation at the field capacity moisture content. *Water Air Soil Pollut.* 114.: 221-250.
- Kandpal, G., Ram, B., Srivastava, P.C. (2004) Transformation of cadmium in soils treated with Cd-enriched sewage sludge and CdCl₂ under field capacity and flooding moisture regimes. *Chem. Speciation Bioavailability.* 16: 111-117.
- Lim, T.T., Tay, J.H., Teh, C.I. (2002) Heavy metals in the environment; Contamination time effect on lead and cadmium fractionation in a tropical coastal clay. *J. Environ. Qual.* 31: 806-812.
- Lu, A., Zhang, S., Shan, X.Q. (2005) Time effect on the fractionation of heavy metals in soils. *Geoderma.* 125: 225-234.
- Ma, Y.B., Uren, N.C. (1998) Transformations of heavy metals added to soil- application of a new sequential extraction procedure. *Geoderma.* 84: 157-168.
- Singh, J.P., Karwasra, S.P.S., Singh, M. (1988) Distribution and forms of copper, iron, manganese, and zinc in calcareous soils of India. *Soil Science.* 146: 359-366.

PHYTOFILTRATION OF ARSENIC CONTAMINATED WATER USING *HYDRILLA VERTICILLATA*

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INTRODUCTION

Arsenic (As) is a ubiquitous metalloid present in the soils, rocks, and natural waters. The irrigation of agricultural soils with As-contaminated groundwater is likely to cause the accumulation of As in both soils and plants, thereby elevating the transfer of As to the food chain, which poses long term risks to human health. Phytoremediation is a solar driven technology with low cost and hence might be suitable for cleaning up of the widespread As contamination. Water thyme (*Hydrilla verticillata*) is a worldwide distributed aquatic weed having fast growth rate and has been demonstrated to be an accumulator of As (Srivastava and D'Souza, 2009). In the present investigation, its ability for As accumulation has been established through exposure to simulated As-contaminated water as found in the regions of Indian subcontinent.

METHODS

Plant material and treatment conditions

Hydrilla verticillata plants were used as the experimental system. The plants were grown in total 8 L of simulated As-contaminated water containing 1500 $\mu\text{g L}^{-1}$ As (Stüben et al., 2003) for 45 days. At 15 days interval, 3 replicates were harvested for analysis of As accumulation in plants and water and for other biochemical assays. Besides, total fresh and dry plant biomass was also measured at each harvesting time.

Determination of arsenic

Total As in the plant material was estimated after digestion of oven-dried plants (100 mg) in 1 mL of concentrated HNO_3 on a heating block at 180°C for 1 h and subsequently at 200°C for 45–60 min so as to evaporate the samples to dryness. The residue was taken up in 10 mL milli-Q water. Water samples were analyzed directly without any digestion. Arsenic concentrations were determined on an ICP-AES.

Determination of hydrogen peroxide and lipid peroxidation

For hydrogen peroxide (H_2O_2) determination, 0.5 ml of 0.5% (w/v) trichloroacetic acid (TCA) extracted plant sample was mixed with 0.5 mL 100 mM potassium phosphate buffer (pH 7.0) and 1 mL of freshly prepared 1 M potassium iodide. Reaction was allowed to develop for 1 h in dark and absorbance was measured at 390 nm. Lipid peroxidation was determined by the estimation of the malondialdehyde (MDA; ϵ of 155 $\text{mM}^{-1} \text{cm}^{-1}$) content.

Assay of antioxidant enzymes

Control and As exposed plants were homogenized in 100 mM chilled potassium phosphate buffer (pH 7.0) containing 0.1 mM EDTA, 1% PVP (w/v) and 2.5% glycerol at 4°C. Homogenate was centrifuged at 15,000 $\times g$ for 15 min at 4°C. The activities of guaiacol peroxidase (GPX; EC 1.11.1.7), catalase (CAT; EC 1.11.1.6) and ascorbate peroxidase (APX; EC 1.11.1.11) were assayed following the standard protocols.

RESULTS AND DISCUSSION

(a) Dry matter yield and arsenic uptake by *Hydrilla* plant

Total dry matter yield of plants was found to increase from the initial 10 g at 0 d to 22 g at 45 d. The As uptake was also increased with an increase in exposure duration (195 $\mu\text{g g}^{-1}$ dw at 15 d to 388 $\mu\text{g g}^{-1}$ dw at 45 d) (Fig 1A). The accumulation data showed that total As removal from contaminated water (8 L water contained a total of 12000 μg As at a concentration of 1500 $\mu\text{g L}^{-1}$) at 45 d was 8546 μg (Fig. 1B).

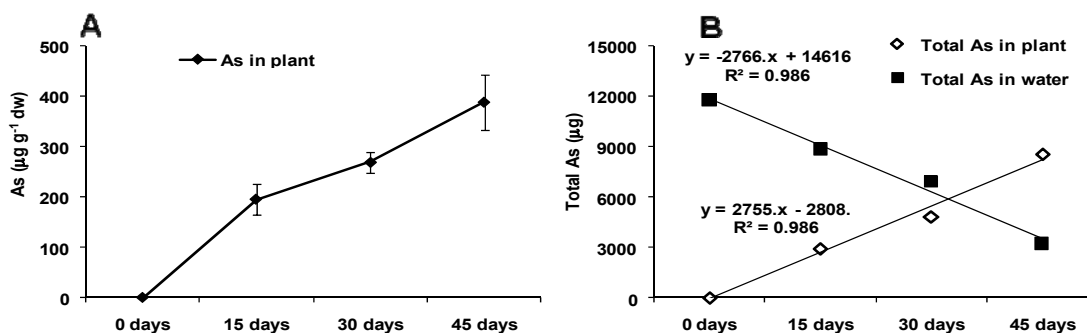


Fig.1. Accumulation of arsenic by *Hydrilla verticillata* grown in simulated As-contaminated water for 45 d (A) and total As in plants and water interpolated for whole plant dry biomass and total volume of water (B). All values are means of triplicates \pm S.D.

(b) Effect of arsenic accumulation on antioxidant enzymes in *Hydrilla* plant

Results showed that hydrogen peroxide and MDA did not demonstrate any significant change in comparison to control (Table 1) suggesting that plants did not experience any toxicity during such a prolonged exposure to As. The activities of GPX and APX (Table 1) increased significantly on all sampling periods by more than 2-fold, however the activity of CAT was not altered significantly except at 30 d (Table 1).

Table 1. Effect of As on oxidative stress parameters and antioxidant enzymes activities

Parameter	Duration					
	15 days		30days		45 days	
	Control	Arsenic	Control	Arsenic	Control	Arsenic
H ₂ O ₂ ($\mu\text{mol g}^{-1}$ fw)	12.1 \pm 0.6	12.8 \pm 0.1	12.1 \pm 0.3	10.6 \pm 0.4	12.19 \pm 0.50	10.5 \pm 0.6
MDA ($\mu\text{mol g}^{-1}$ fw)	85.5 \pm 7.9	96.4 \pm 9.6	87.5 \pm 7.1	93.6 \pm 4.5	82.57 \pm 12.7	70.9 \pm 11.9
GPX (units mg ⁻¹ protein)	2.4 \pm 0.6	6.5 \pm 1.2	2.5 \pm 0.1	5.2 \pm 0.4	3.18 \pm 0.88	7.6 \pm 1.6
CAT (units mg ⁻¹ protein)	8.5 \pm 0.9	10.3 \pm 1.2	6.3 \pm 0.8	15.2 \pm 2.8	7.14 \pm 1.88	8.2 \pm 0.4
APX (units mg ⁻¹ protein)	1.2 \pm 0.18	3.5 \pm 0.6	1.2 \pm 0.2	3.1 \pm 0.6	1.45 \pm 0.06	3.1 \pm 0.4

CONCLUSIONS

The present study demonstrates that hydrilla plants are not only capable of accumulating significant amounts of As (8546 $\mu\text{g As g}^{-1}$ dw within 45 days) but also effectively tolerate As stress through significant stimulation of antioxidant enzyme activities.

REFERENCES

- Srivastava, S. and D'Souza, S.F. (2009). Increasing sulfur supply enhances tolerance to arsenic and its accumulation in *Hydrilla verticillata* (L.f.) Royle. *Environ. Sci. Technol.* 43: 6308-6313.
- Stüben, D., Berner, Z., Chandrasekharam, D. and Karmakar, J. (2003) Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing conditions. *Appl. Geochem.* 18: 1417-1434.

DISCOVERING PLANT-BACTERIAL INTERACTION TO CLEAN UP PETROLEUM CONTAMINATED SOIL

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INTRODUCTION

Petroleum, the backbone of any country, has now become a threat to the environment as leaking of storage tanks, pipelines and accidental spill jeopardize the environment as petroleum products contain carcinogenic aromatic compounds. Rhizoremediation is getting attention compared to sole use of either microorganism or plant. The challenging task is to isolate such microorganisms that are not only acclimated to xenobiotic environment but also have synergistic relationship with the plants in stressed condition. Plant growth promoting rhizobacteria (PGPR) having 1-aminocyclopropane-1-carboxylic acid ACC-deaminase activity are reported to help the plant in stressed environment by reducing stress induced ethylene (Glick et al., 1998). To study this, microorganisms were isolated from petroleum contaminated soil samples from different agroclimatological zones of Pakistan having average temperature range from 25°C to 40°C. These isolates were tested for ACC-deaminase activity and bioremediation capability. Isolates having dual character viz. ACC-deaminase activity and bioremediation were further tested by inoculation to plants to observe their possible effect on plant growth.

METHODS

ISOLATION OF MICROORGANISMS

Selective mineral salt medium was used to isolate microorganisms. Five grams of soil from each soil sample were dissolved in distilled sterile water and shaken at 100 rpm. Growth medium for microorganisms on agar plates was mineral salt medium (MSM) (Supaphol et al., 2006) amended with 2.5ml of filter sterilized crude oil (kerosene, diesel and gasoline) as sole source of carbon. Morphologically different colonies growing on selective medium were picked up and further streaking was carried out on the same growth medium.

BIOREMEDIATION ASSAY

Twenty four well microtitre plates were used for bioremediation assays to determine the PAH and crude oil degrading ability of the isolates. Mixture of PAHs and crude oil were used as test compounds in separate plates. Two hundred microlitre of indicator p-Iodonitrotetraazolum (p-INT) was added in each well. These plates were incubated at room temperature for three weeks. The bacterial inoculated wells that turned red were attributed to have PAH and crude oil (mixture of kerosene, diesel and gasoline) degrading bacteria (Hanson et al., 1993)

ACC-DEAMINASE ACTIVITY

ACC-deaminase activity was measured according to a modification of the method of Honma and Shimomura (1978) and Penrose and Glick (2003) which measures the amount of α -ketobutyrate produced when the enzyme ACC-deaminase cleaves ACC. The number of nmol of α -ketobutyrate produced by this reaction was determined by comparing the absorbance at 540nm of a sample to a standard curve of α -ketobutyrate ranging between 0.1 and 1.5 μ mol. Twenty seven isolates were found with bioremediation capability along with ACC-deaminase activity. These Twenty seven isolates were inoculated to alfalfa plant to screen best isolates regarding plant growth parameters.

PLANT GROWTH PROMOTING ACTIVITY OF SCREENED ISOLATES

In a growth chamber, jar trials under axenic and controlled light and temperature were conducted on alfalfa plant to assess the plant growth promoting activity of selected isolates. For inoculation, a seed slurry method was used. Half strength Hoagland solution was used

for nutrients twice a week. After 60 days, plants were harvested and growth parameters such as root shoot length, fresh biomass and oven dried biomass were recorded.

RESULTS AND DISCUSSION

Table 1. Screening of microbes having ACC-deaminase activity and bioremediation capability.

Isolate Name	ACC-deaminase activity (α -ketobutyrate nmol g ⁻¹ biomass hr ⁻¹)	Bioremediation Assay
PM32Y	1334.15	++++
SFD2S2	1027.28	++
WZ3S1	268.76	++++
JM44	212.08	+++
MZT72	175.46	++
SP104Y	112.51	+++
SM73	96.91	++++
WZ3S3	107.63	++++

About 300 isolates were initially isolated from petroleum contaminated soil samples. Out of these three hundred isolate only 27 isolates were selected on the basis of positive result in bioremediation and ACC-metabolism assays. These 27 strains were used to inoculate the alfalfa seeds in jar trials. Eight bacterial strains, with ACC-deaminase activity and bioremediation capability (Table 1) showed promising positive relationship with plants. Our results revealed that bacterial isolates PM32Y increased the fresh biomass of alfalfa by 154% as compared to uninoculated control. This dramatic increase in the upper part of plant may be attributed to increase in root biomass which was 91% compared to un-inoculated control plants. Rhizobacteria usually enhance root growth (Bertrand et al., 2000) and this interaction with the roots can trigger increased biomass production and crop yield (Vessey , 2003)

This synergistic relationship between plant and bacteria may be helpful in establishing rhizoremediation as the bioremediation assay also showed that the bacterial isolate PM32Y have strong ability to biodegrade PAHs and crude oil component such as kerosene, gasoline and diesel.

CONCLUSION

Synergistic use of bacteria and plants may be a better approach to handle on-site petroleum contamination of soils.

REFERENCES

- Bertrand, H., C. Plassard, X. Pinochet, B. Touraine, P. Normand and J.-C. Cleyet-Marel. 2000. Stimulation of the ionic transport system in *Brassica napus* by a plant growth-promoting rhizobacterium (*Achromobacter* sp.). *Can. J. Bot.* 46: 229–236.
- Glick, B.R., D.M. Penrose, J. Li. 1998. A model for lowering of plant ethylene concentration by plant growth promoting bacteria. *J. Theor. Biol.* 190: 63-68.
- Hanson, K.G., D. Jitendra and A.J. Desai, A rapida nd simple screening technique for potential crude oil degrading microorganisms. *Biotech. Tech.* 7:745- 748.
- Honma, M. and T. Shimomura. 1978. Metabolism of l-aminocyclopropane-1 -carboxylic acid. *Agric. Biol. Chem.* 42: 1825-1831.
- Penrose, D.M. and B.R. Glick. (2003). Methods for isolating and characterizing ACC deaminase-containing plant growth promoting rhizobacteria. *Physiol. Planta.* 118: 10-15.
- Supaphol, S., S. Panichsakpatana, S. Trakulnaleamsai, N. Tungkananuruk, P. Roughjanajirapa A.G.Donnell. 2006. The selection of mixed microbial inocula in environmental biotechnology: Example using petroleum contaminated tropical soils *J. Microbiol. Methods* 65:432– 441.
- Vessey, J.K. 2003. Plant growth promoting rhizobacteria as biofertilizers. *Plant Soil* .255: 571–586.

ARSENIC BIOREMEDIATION POTENTIAL OF *Variovorax* SP. MM-1 ISOLATED FROM SOIL

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INTRODUCTION

Arsenic (As) contamination in surface and groundwater is a serious environmental problem worldwide that results both from natural sources and anthropogenic activities. In recent years chronic exposure to higher doses of As has caused widespread arsenicosis in several parts of the world especially in Bangladesh and India (Rahman et al. 2009). Arsenic exists in several oxidation states in the environment but the most abundant forms are arsenite (AsIII) and arsenate (AsV). AsIII is more mobile in aqueous solution and about 100 times more toxic than AsV (Al-abed et al. 2007). Several arsenic removal technologies are currently available which target the removal of AsV following a chemical pre-oxidation. The major disadvantages of such techniques are the generation of additional pollutants and high cost. Microorganisms are known to play an important role in geochemical cycling of arsenic of which several bacteria are involved in transformation processes like oxidation, reduction and methylation (Silver and Phung 2005). Bacterial oxidation of AsIII represents either a potential detoxification mechanism or energy derivation for growth-supporting metabolism which is catalysed by a periplasmic enzyme, arsenite oxidase (Cai et al. 2009). Although a number of bacterial strains have been isolated since the first report by Green (1918), most of them are slow oxidizers and their physiological role is not well understood. For effective bioremediation of arsenic, it is important to know the diversity of arsenic oxidizing bacteria as well as to explore their oxidation efficiency. In this study, we have isolated a rapid arsenite oxidizing bacteria from a heavy metal contaminated environment. The isolated strain was phylogenetically identified and the arsenite oxidation ability was assessed.

METHODS

Heavy metal contaminated soil was collected from South Australia which contains lead (562 mg/kg), zinc (902 mg/kg), manganese (305 mg/kg) and 8 mg/kg of arsenic. One gram of soil was inoculated into minimal salts (MS) medium (Santini et al. 2000) supplemented with AsIII as NaAsO₂ and 0.5% (w/v) glucose aerobically for 1 week at 25°C. The resulting enriched cultures were then serially diluted and plated on MS agar media containing the same concentration of arsenite. Single colonies were picked, restreaked several times to purify and tested their abilities to oxidize AsIII in MS media. The strain which showed higher ability to oxidize AsIII was then used for phylogenetic identification and determination of AsIII oxidation activity. For AsIII oxidation assay, overnight grown culture in MS medium containing AsIII was harvested and aliquot of concentrated culture was inoculated into the same medium with 0.1 mM (7.5ppm) and 1mM (75 ppm) of AsIII. All incubations including controls were performed in duplicate. At the selected time interval, aliquots of the medium were taken for measuring the cell optical density and for As speciation following centrifugation. The concentration of AsIII and AsV were determined by ICP-MS. Genomic DNA was isolated using a genomic DNA prep kit (Bioline). PCR amplification of 16S rRNA gene was performed in a gradient thermal cycler (Bio-Rad) using universal primers and the gene sequencing was detected on an ABI 3130 Sequencer (Applied Biosystems) from Southpath and Flinders Sequencing Facility.

RESULTS AND DISCUSSION

A number of strains were capable of growing on the media containing AsIII. Among them three strains showed the ability to oxidize AsIII. All the isolated organisms were characterized as aerobic and gram negative. The nucleotide blast search result of the 16S rRNA gene sequence for the best oxidizing isolate MM-1 (1407 bp) indicates that the strain belongs to the genus *Variovorax* with 99% similarity to *Variovorax paradoxus*. The experimental results showed that the strain started the AsIII oxidation in the lag phase with cell density 0.04 (OD₆₀₀) and completely oxidized 1 mM arsenite to arsenate within 4 h before proceeding into growth phase (Fig. 1). The generation time of the isolate MM-1 in MS media is 14.5 h (without As) and 34 h (with 0.5 mM AsIII). This rapid oxidation ability of the tested strain was due to the presence of very efficient arsenite oxidase enzyme in the membrane. The strain could grow and oxidize in pH range 5-9 while the initial optimum pH is 7. The other carbon sources such as dextrose, fructose, maltose, sucrose and mannitol also support growth and arsenic oxidation by this strain.

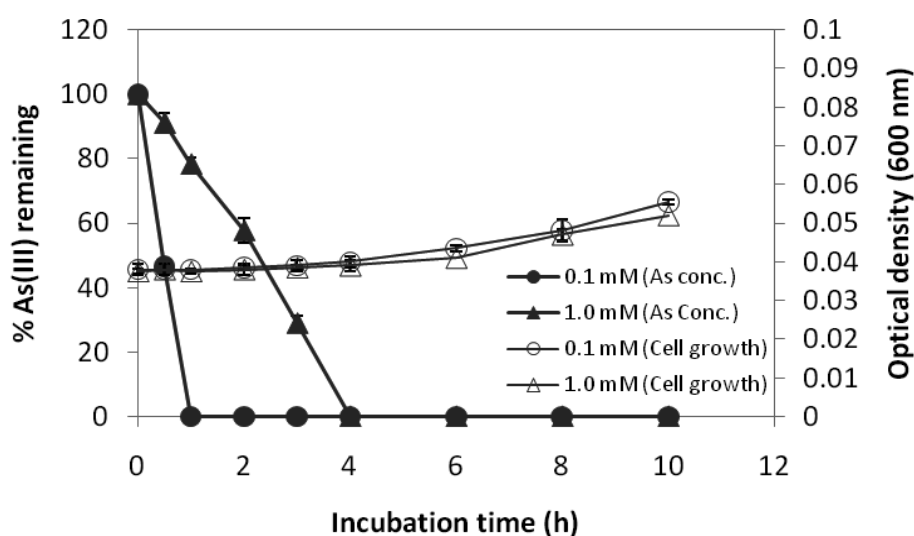


Fig. 1: AsIII oxidation and culture density during aerobic incubation of MM-1

CONCLUSIONS

The isolated bacterial strain, *Variovorax* sp. MM-1 exhibited exceptional ability to oxidize AsIII to AsV when compared with previously isolated strains. This novel strain has great potential for bioremediation of arsenic contaminated water/soil.

REFERENCES

- Al-Abed, S. R., Jegadeesan, G., Purandare, J. and Allen, D. (2007) Arsenic release from iron rich mineral processing waste: influence of pH and redox potential, *Chemosphere*. 66:775-782.
- Cai, L., Liu, G., Rensing, C. and Wang, G. (2009). Genes involved in arsenic transformation and resistance associated with different levels of arsenic-contaminated soils, *BMC Microbiol.* 9:4.
- Green, H. H. (1918) Description of a bacterium that oxidizes arsenite, and one which reduces arsenate to arsenite from a cattle-dipping tank, *South Afr J Sci.* 14:465-467.
- Rahman, M., Naidu, R. and Bhattacharya, P. (2009), Arsenic contamination in groundwater in the Southeast Asia region, *Environ Geochem Health.* 31:9-21.
- Santini, J. M., Sly, L. I., Schnagl, R. D. And Macy, J. M. (2000) A new chemolithoautotrophic arsenite-oxidizing bacterium isolated from a gold mine: phylogenetic, physiological and preliminary biochemical studies, *Appl Environ Microbiol.* 66:92-97.
- Silver, S. and Phung, L. T. (2005) A bacterial view of the periodic table: genes and proteins for toxic inorganic ions, *J Ind Microbiol Biotechnol.* 32:587-605.

RECENT ADVANCES IN THE REMEDIATION OF SOIL AND GROUNDWATER IMPACTED BY CHROMIUM ORE PROCESSING RESIDUE

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INTRODUCTION

Historically, chromium was recovered from chromite ore in many industrial countries for use in steel production, tanning, and wood preservation treatment. This process typically consisted of mixing dry-milled ore with lime (CaO) and soda ash (Na₂CO₃) followed by high-temperature roasting to promote oxidation of trivalent to hexavalent chromium. The chromium was then recovered primarily in the form of soluble sodium chromate (Na₂CrO₄) by countercurrent leaching which produced a high-lime chromium ore processing residue (COPR).

This waste byproduct contained typically 2 to 7 percent chromium by weight due to incomplete oxidation of the ore and incomplete leaching of chromate. The high-pH chromite process generated millions of tons of COPR in North America, Western Europe, and Australia, and is still being used in Eastern Europe and Asia.

This waste material was often sold or donated as construction aggregate to be used as backfill, wetlands fill, grading for road construction, building foundations, and pipeline construction. This highly-alkaline waste material is known to leach toxic and soluble hexavalent chromium impacting soil, groundwater, and surface waters. This leachate with high levels of hexavalent chromium, an allergen, mutagen, phytotoxin and known human carcinogen, poses significant risks to human health and the environment.

METHODS

Many COPR legacy sites exist around the globe from Hudson County New Jersey USA to Southeast Glasgow, Scotland. One such site in Australia is the former Stauffer Chemical Plant, Camellia (Sydney) NSW. These sites have often been created by the incorporation of the COPR material into fill, upon which developments from football pitches to airports have been constructed.

COPR has proven a difficult waste to treat and remediate due to the nature of mineral phase retention, high concentrations of Cr(VI), complexities of leaching mechanisms, and high pH conditions. Traditional chemical reductants used for treating soil, water, and wastewater such as zero valent iron, ferrous iron, organic materials, and/or reduced sulfur species, developed for acidic to neutral pH conditions, have often met with limited success when applied to the highly-alkaline COPR waste. Some conventional treatments have resulted in severe heaving of soils and even increased leaching of Cr(VI). Although intercepting hydrological pathways to treat dissolved Cr(VI) can be effective for containment and mitigating risk, the absence of source treatment means that such systems would require operation into perpetuity.

Extensive mineralogical analysis of COPR using XRF spectroscopy and X-Ray Powder Diffraction (XRPD), and leaching tests have been conducted to better characterize COPR at two of the world's major sites of historical contamination, in Hudson County, New Jersey and Southeast Glasgow, Scotland. These studies have helped to identify some of the problems in applying conventional methods of reductive treatment to such material.

RESULTS AND DISCUSSION

However, subsequent laboratory testing in 2005 at the University of Wisconsin-Madison and the University of Edinburgh independently confirmed the potential for successful treatment of COPR using polysulfide reagents. More recent field testing and applications at these two areas impacted by COPR, have confirmed this success. In particular, aboveground skip trials as well as in-situ trials conducted in Glasgow have provided a better understanding of leaching mechanisms and show promise for full-scale remediation.

At the latter site, the challenge for remediation primarily resides in the deliverability of polysulphide for treatment of significant volumes of COPR deposited below the water table at depths of 10m or greater, particularly based on its reactivity and the potential for precipitation as a result of the reaction products. Three specific techniques, a five-point recirculation approach, direct injection and deep soil mixing are therefore currently being trialled at Glasgow to assess their efficacy in delivering calcium polysulphide to the area of concern.

REMEDICATION OF A SPENT PHOSPHORIC ACID CATALYST WASTE SITE USING STABILISATION AND PHYTOREMEDIATION

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INTRODUCTION

Over a 19 year period, an oil refinery in New South Wales (NSW) disposed of spent phosphoric acid (SPA) catalyst waste in an on site landfill. Prior to disposal, the SPA was treated with limestone in an attempt to neutralise the material and prevent leaching of acidic liquid waste into the environment. The landfill was not lined and the underlying geology comprises medium grained Quaternary sandy deposits overlying sandstone bedrock at depths of 6 to 10 metres below ground level (mbgl). The sandy deposits host an unconfined aquifer with standing water levels between 1 and 2 mbgl. The SPA waste has subsequently resulted in a significant plume of low pH groundwater contamination, with the principal contaminants being dissolved phase phosphate and total petroleum hydrocarbons (TPH). The resultant contaminant plume has migrated approximately 200 metres down-gradient of the waste site towards a wetland environment.

METHODS AND RESULTS

Prior to devising a remediation strategy for the site, a desk top review was undertaken of existing information including previous assessment reports and feasibility studies. This information was used to plan the establishment of additional groundwater monitoring locations for further assessment of the extent of the plume. Groundwater monitoring was undertaken from 20 wells across the extent of the plume for assessment of geochemical parameters (including pH, electrical conductivity, reduction-oxidation potential and dissolved oxygen), contaminants of potential concern (including TPH and phosphate) and other key chemical parameters including major cations and anions and metals.

The results of the groundwater monitoring were used for assessment of current levels of contamination and were compared to relevant health and ecological screening criteria endorsed by the NSW Department of Environment, Climate Change and Water (DECCW). The results were also used to conduct a hydrogeochemical assessment to determine the chemical speciation of the dissolved ions and for prediction of mineral phases that are likely to precipitate from solution based on the water chemistry. Modelling was conducted using MINTEQA2, a thermodynamic aqueous geochemical modelling application (Allison, *et al.*, 1990). An understanding of the groundwater chemistry was considered a key aspect of selecting a pragmatic remedial solution for the site that was also protective of human health and the receiving ecological communities. A key result of this assessment was the predicted oversaturation of phosphate mineral phases, indicating that these minerals are likely to precipitate from solution. Saturation indices for key phosphate mineral phases are presented in Table 1. Positive saturation indices indicate precipitation of mineral phases.

Table 1. Saturation indices for phosphate mineral phases predicted using hydrogeochemical modelling (MINTEQA2)

MWID	CaHPO ₄ (s)	Hydroxyapatite Ca ₅ (PO ₄) ₃ (OH)	MnHPO ₄ (s)	Vivianite Fe ₃ (PO ₄) ₂ ·8(H ₂ O)
GHDMW2	-2.318	-2.592	1.631	-0.431
PMW31	0.183	5.413	3.400	3.547
PMW32	-0.157	2.076	3.150	2.372
SPAMW1	-1.883	-2.301	2.144	3.232
SPAMW8	-2.458	-4.040	1.223	0.872
SPAMW16R	-0.895	1.992	2.756	3.113

REMEDIAL STRATEGY

Any remedial strategy selected for the site would need to address two key issues, i.e. the contaminant source area and the extensive dissolved plume of contamination. A combined remedial approach was selected to discretely treat these two issues in a sustainable manner. The first approach was to stabilise and contain the contamination in the source area to prevent any further leaching or release of contaminants to the environment. Methods for source containment included capping, in situ treatment and ex situ removal. The most effective solution in terms of cost and contaminant reduction was considered to be in situ treatment and containment using a neutralising agent capable of permanently fixing the contaminants to prevent any further leaching. Finely crushed limestone was chosen as the neutralising agent for treatment after conducting laboratory trials with various alkaline materials (HRL, 2006).

The groundwater results indicated that the contaminant plume posed no current risk to human health or the receiving environment. Therefore a passive approach was adopted for treating the groundwater contamination by using phytoremediation. Using fast growing, hydrophilic tree species such as poplars or willows, a passive method can be employed to remediate the dissolved contaminants. Hybrid non-propagating tree species are typically chosen for use in phytoremediation.

A remedial action plan (RAP) was prepared for the site evaluating different remedial approaches, providing a rationale and conceptual design for the chosen approach and defining remedial goals. The RAP was submitted to the local Council for endorsement as part of a development application for the proposed remedial works.

CONCLUSIONS

A pragmatic remedial strategy has been developed for the SPA catalyst waste site to achieve compliance with remedial goals and prevent further impact to the receiving environment. The remediation at the site is currently underway.

REFERENCES

- Allison, JD, Brown, DS and Novo-Gradac, KJ, 1990. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. Athens, GA: Environmental Research Laboratory, Office of Research and Development, United States Environmental Protection Agency. Report No. EPA/600/3-91/021.
- Coffey (2006) *Contamination Assessment, Limestone Pits, Caltex Refinery, Kurnell*. Report reference: E12258/10-AK. 7 August 2006.
- HRL (2006) *Treatment of Spent Catalyst Waste from Caltex Petroleum Australia Ltd*. HRL Technical Memorandum No 0841. 7 December 2006.

SUSTAINABLE REMEDIATION SOLUTION FOR LEAD SHOT IMPACTED RECREATIONAL RESERVE: MECHANICAL SIEVING AND GRAVITY SEPARATION

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INTRODUCTION

This study presents the findings of a field-scale trial of a sustainable treatment approach utilizing mechanical sieving and gravity separation to remediate a lead shot impacted recreational reserve in Victoria, Australia.

Shallow surface soils at the recreational reserve have been impacted by lead shot pellets, from the historical use as a trap and skeet gun club for some 60-70 years. The potential risks presented by the lead shot impacted soil to recreational users were investigated, leading to the development of a remediation action plan (RAP), including a detailed options assessment. The remediation evaluation compared five options: (1) off-site disposal, (2) soil washing, (3) soil vacuuming, (4) capping of impacted soils in-situ and (5) mechanical sieving with gravity separation. Due to significant community interest in the project, the remediation options assessment was evaluated using GoldSET®, a sustainable options decision-making tool (Ehrman and Wallis 2011).

Mechanical sieving with gravity separation was identified as the preferred option based on the selection of key project remediation objectives including i) minimising disruption to existing community recreational users, ii) minimising the generation of expensive hazardous wastes, iii) minimising the need for ongoing management and iv) maximising the flexibility of future site uses.

The preferred technology provider indicated their equipment could remove lead shot from soil; however they could not provide verification data as proof of treatment. A field trial was therefore designed to verify whether the technology could remove sufficient mass of lead shot from the site to satisfy the project remediation objectives.

METHODOLOGY

The contractor's mechanical and gravity separation process was based on removal of lead shot pellets through physical sieving separation and gravity separation using adjustable vertical air blowers. A performance criterion of 90 percent lead shot count removal from soil was agreed as part of the project RAP.

The repetitive nature of shooting at trap and skeet fields results in a relatively predictable area of shot fall where the majority of lead shot will be encountered (ITRC, 2003). The visually observed distribution of lead shot at the former gun club was found to be consistent with the theoretical shot fall zone, with the lead impact zone estimated to be 16,500 m². In addition, the vertical distribution of lead shot, in clay based soils, was found to be less than 0.1 metres below ground level (mbgl). The field trial was conducted on a transect (1.2 m x 50 m) of silty clay soils with the highest density of lead shot in soil at the site.

Soil samples (approximately 1.5 kg dry mass) were collected on a 2.5 m grid pre- and post-treatment. Soils were treated to a depth of 0.1 mbgl. The number of lead shot within pre- and post-treatment samples was determined by washing soils through a 2.36 mm analytical grading sieve.

RESULTS AND DISCUSSION

The results of the field trial are shown in Figure 1.

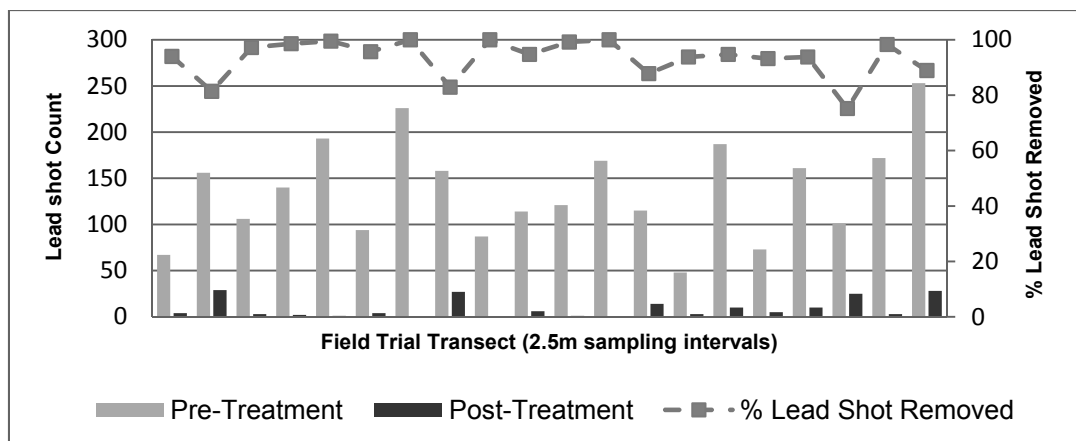


Fig. 1. The number and percentage of lead shot pellets removed from surface soils (0.1 mbgl) after one treatment run with the mechanical/gravity separation machine.

The trial indicated that the soils treated by mechanical/gravity separation can remove over 90 percent of lead shot count (>2.36 mm in diameter) and thereby remove the bulk lead shot, the soil at this particular site could be remediated to a National recreational land use guideline for total lead of 600 mg/kg (based on an average mass of 89 mg/ lead shot pellet). During the field trial the technology was assessed to operate at a feed rate of approximately 100-200 kg/ hour depending on the moisture condition of soil, obstructions including density of plant rooting systems and depth of machine cut. Pre-treatment of lead shot impacted soil with a rotary hoe and/or herbicide was found to improve the percentage of lead shot removal, by creating a more friable soil with minimal large soil clods. Treatment of the trial area removed approximately 150 kg of lead shot from a treatment volume of approximately 6 cubic metres. It is estimated that some 5 - 15 tonnes of lead shot could be removed from the soil for offsite recycling from the remediation process.

There is estimated to be nearly 300 gun clubs around Australia, of which approximately 60 are located in Victoria. The cost of disposal of lead shot impacted soil to a regulated landfill in Victoria, for a small club with three shooting traps, is estimated to be between \$2-5 Million. The relatively high remediation cost for these typically low value sites present a challenge to address economic, environmental and social needs of the communities in which they are located, particularly when a change in land use is demanded.

CONCLUSIONS

Mechanical/gravity separation can successfully remove over 90 percent of lead shot pellets from insitu soils, thereby removing the bulk of the soil contamination and minimising the generation of waste soils for offsite disposal. However, effective separation of lead shot from the soil using dry mechanical/gravity separation is reduced where soils are too wet or have high vegetation matter with dense root systems. In addition, the treated soils are not suitable for all sensitive uses, as trace lead shot pellets remain which may require some additional management, such as installation of a separation layer between users and the trace lead shot pellets. The field trial demonstrated that the selected technique is a relative low-cost, effective method for cleaning up lead shot impacted soils, which also allows the lead shot to be recovered and recycled offsetting some of site remediation costs.

REFERENCES

ITRC (2003). *Characterization and Remediation of Soils at Closed Small Arms Firing Ranges*. Interstate Technology and Regulatory Council (ITRC). January 2003.

Ehrman C. and Wallis C. (2011). *GoldSET® Evaluating Options Sustainably Groundwater, Soil and Waste Case Studies*. Australian Technology Park Sydney. EcoForum 9 – 11 March 2011.

SHALLOW VADOSE ZONE SOIL GAS SAMPLING FOR VAPOUR INTRUSION RISK ASSESSMENT

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INTRODUCTION

Soil gas sampling is the most preferred approach for vapour intrusion (VI) risk assessment of volatile organic compound (VOC) present both in unsaturated subsurface or groundwater contaminated sites. However soil gas sampling should be carefully evaluated regarding where, when and how many samples should be collected for accurate risk assessment on VI (USEPA, 2002, Wong and Agar, 2009). The spatial distribution of soil gas varies greatly due to heterogeneity of transport media (vadose zone) both laterally and vertically. The exact location of soil gas sampling around a building is a site specific decision based on preferential path and plume delineation and a number of other factors. However the depth at which soil gas sampling should be taken depends on soil properties and climatic conditions. It may be necessary to collect soil gas samples at multiple time intervals for a minimum of one year to compensate for the effects of weather as near surface vadose zone shows large temporal variation in soil gas concentrations (Hers et al., 2002, McHugh et al., 2007). Vapour intrusion studies at depths shallower than 1m below ground surfaces for risk assessment should be carefully evaluated for stable and repeatable measurements. Soil gas in the unsaturated zone varies with climate and soil hydraulic properties such as air permeability. In this study, we investigate the effect of soil type, seasonal variations and depth of sampling on VOC at contaminated site.

METHODS

Site characterisation and plume delineation of trichloroethylene (TCE) was investigated to address the potential vapour intrusion health risk at a chlorinated solvent contaminated land in South Australia. The study was designed to investigate concentration gradients in the soil profile at shallow depths above a plume and the influence of soil moisture and temperature variations. The site was instrumented for soil gas sampling from 5 nested soil vapour implants installed in groups of three at 1 m, 2 m and 3 m depths. Soil gas samples were taken using a Tedlar® bag as per USEPA 8260 TO-15 method. Samples were analysed within 24 hr using head space auto-sampler Gas Chromatograph.

RESULT AND DISCUSSION

Characterisation of lateral and vertical soil gas concentration at the site shows horizontal plume delineation typically from North-east to South-west (Fig 1). Soil gas concentration contour plot at three depths 1 m, 2 m, & 3 m shows direction of soil gas plumes at all depth towards south-west during sampling seasons; contour plot at each depth demonstrates strong correlations of soil gas concentration along vertical profile. Vapour concentration decrease at shallower depths. Soil moisture and temperature measured at 3 m for the SGW13 & SGW23 shows little change (Fig 3). Significant variation of soil gas concentration is observed at up to 3 m depth with an order of magnitude change over the 4 month (January to April) monitoring period (Fig 2).

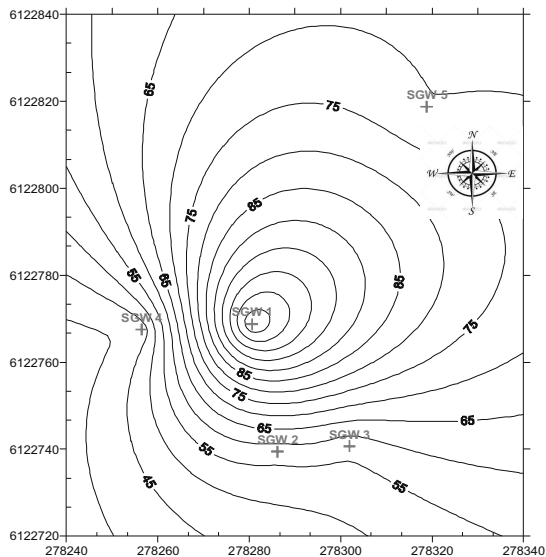


Fig 1. Contour plot of vapour plume delineation at 3 m depth (values are ppmv)

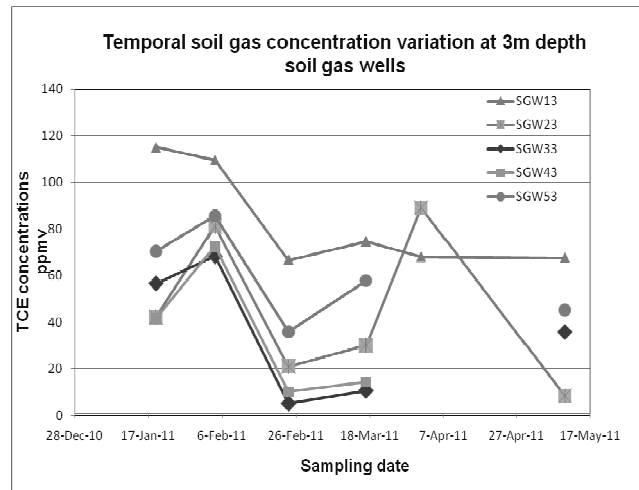


Fig 2. Temporal soil gas concentration variation at 3 m depth soil gas wells

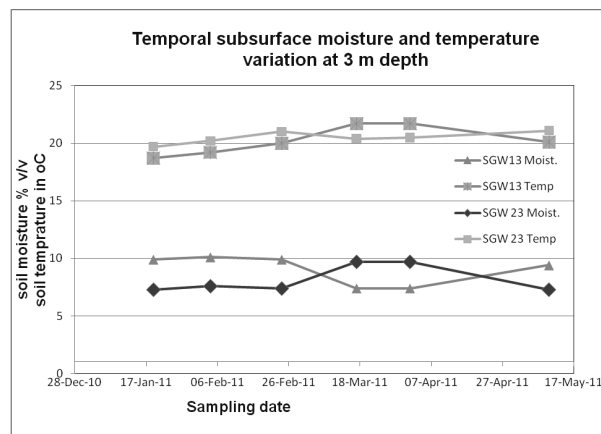


Fig 3. Temporal subsurface moisture and temperature variation at 3 m depth

CONCLUSIONS

It is evident from our study that application of shallow vadose zone soil gas sampling in risk assessments and screening of VOC sites can result in significant uncertainty due to the large variability in soil gas concentrations.

REFERENCES

- HERS, I., ZAPF-GILJE, R., EVANS, D. & LI, L. 2002. Comparison, Validation, and Use of Models for Predicting Indoor Air Quality from Soil and Groundwater Contamination. *Journals of Soil and Sediment Contamination* 11, 491 - 527.
- MCHUGH, T. E., NICKELS, T. N. & BROCK, S. Year. Evaluation of Spatial and Temporal Variability in VOC Concentrations at Vapor Intrusion Investigation Sites. *In: Proceeding of Air & Waste Management Association's Vapor Intrusion: Learning from the Challenges*, September 26-28, September 26-28, 2007 Houston, TX 77098-404. 129-142.
- USEPA 2002. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils. *In: EPA OFFICE OF SOLID WASTE & ENERGY RESPONSE* (ed.). Washington D.C.: EPA530-D-02-004.
- WONG, T. T. & AGAR, J. G. 2009. Development of a technically defensible soil gas sampling strategy for vapour intrusion assessments. *Canadian Geotechnical Journal*, 46, 102-113.

STATISTICAL APPROACH TO IMPROVING RELIABILITY AND DEFENSIBILITY OF BIOACCESSIBLE FRACTION ESTIMATION

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INTRODUCTION

Contaminated site investigations generally collect point samples from populations. These generally only a very small portion of the environmental conditions being characterised, including bioaccessible data. In many situation only a small number analysis are performed resulting in uncertainty as to the appropriate bioaccessibility value to adopt in risk assessment. Commonly the maximum measured bioaccessibility factor is used. However, this has a significant limitation that must be considered. When collecting samples from populations it is likely that a small number of bioaccessibility measurements would not characterise the minima and maxima, nor be representative of the variability of the population. Most likely the outcome from analysis of a small number of samples for bioaccessibility is that the results may be representative of the most frequent values from near the mean and / or median of the population distribution.

Monte Carlo simulations offer a robust method for estimating bioaccessibility. This paper focuses on the statistical data evaluation aspects that may prove of value to risk assessors in assessment of an appropriate bioaccessibility factors for risk assessments. Detailed discussion and reasoning of testing methods used are beyond the scope of this paper.

METHODS

Monte Carlo simulations offers an method for expanding the data set base on general population parameters estimated either from samples where sufficient testing was undertaken or conservative generic inputs based on experience at other similar sites and / or published information. A range of population distributions (normal, log-normal, triangle, exponential, beta function etc) are available to represent populations being studied. The beta function has the flexibility to simulate a wide range of populations and requires four essential inputs (population minimum and maximum, alpha and beta shape factors).

- The beta distribution over a range [a, b] is defined by:

$$f(x) = C(x - a)^\alpha (b - x)^\beta$$

Where

- f = the beta function for value x
- C = normalizing constant

$$C = \frac{(\alpha + \beta + 1)!}{\alpha! \beta! (b - a)^{\alpha + \beta + 1}}$$

- a = minimum value of the data range
- b = maximum value of the data range
- α = shape factor 1
- β = shape factor 2

RESULTS AND DISCUSSION

Bioaccessibility testing intends to assist risk assessors in improving their understanding of the risk a contaminant may pose to human health. However, test results are often variable posing the challenge of what value to adopt in the risk assessment. Table 1 presents a

summary of 22 bioaccessibility tests on soils from the same mineralised region. Bioaccessibility of the -250 µm fraction of each test item was measured using a physiologically based extract test (PBET) method (Ruby et al., 1996). While this type of test has demonstrated to produce reasonable reliability for Arsenic, Cadmium and Lead, results for some other metals need to be treated with caution.

Table 1: Data Statistics (%)

	Cr	Mn	Ni	Cu	Zn	As	Cd	Hg	Ti	Pb
mean	3	30	17	24	29	7	23	4	9	21
median	2	32	17	25	30	5	23	3	7	19
StDev	2	10	12	8	9	6	12	3	9	7
min	1	12	2	11	13	2	6	0	0	12
max	12	46	36	43	49	30	46	11	35	37
Model Percentile	75	72	90	78	78	84	99	95	98	96

As can be observed there is considerable variation in the measured bioaccessibility values both with and between the metals. To assist the risk assessors the statistical data parameters were used to develop beta function based Monte Carlo simulations using 10,000 points. As the test range is unlikely to have spanned the entire population range the model assumed a minimum of 0% to a maximum of 100% to allow for rare outliers in the model. As shown on Table 1 the model percentiles that the measured maxima represent are variable and not consistent and thus consistent application of a specific percentile is not achieved by use of maximum values. Adoption of the measured maxima, which is a common practice, would therefore result in very variable inputs to a risk assessment for the various metals. Table 2 presents the bioaccessibility for a range of probability percentiles based on the modelling results.

Table 2: Bioaccessibility Percentiles Based on Monte Carlo Model Results (%)

Percentile	Cr	Mn	Ni	Cu	Zn	As	Cd	Hg	Ti	Pb
50	3	32	18	26	30	6	24	3	7	19
75	5	42	26	32	37	11	33	6	14	25
80	5	44	29	34	39	13	36	7	16	26
95	8	55	41	42	48	22	49	11	28	34
99	12	64	52	49	55	31	59	16	39	41
100*	50	94	88	75	88	75	94	50	88	75

* represents 99.99999th Percentile

As shown in Table 2, the Monte Carlo modelling allows the risk assessor to adopt consistent probability based bioaccessibility factors for risk assessments.

CONCLUSIONS

Developing consistent and defensible bioaccessibility fraction estimates for risk assessments when there is only a limited data set of point samples from large and potentially diverse populations presents a challenge for risk assessors. Use of Beta function based Monte Carlo simulations can develop large data sets that are more representative of the real population distribution and allow for adoption of probability based bioaccessibility factors. As the example data set illustrated measure bioaccessibility factors are variable and the common practice of using the maximum measured value may not be representative of an upper bound value. Using Monte Carlo simulations allow for estimating bioaccessibility factors at various probabilities and selecting the desired percentile for risk assessment, resulting in a more consistent and defensible risk assessment approach.

BIOACCESSIBILITY OF Pb IN DIFFERENT PARTICLE SIZE FRACTIONS IN LONG-TERM FIELD CONTAMINATED SOILS: IMPLICATIONS FOR HUMAN HEALTH RISK ASSESSMENT

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INTRODUCTION

Soil contamination from lead (Pb) is a widespread phenomenon. Urban soils are well known to be enriched with Pb as a result of Pb-petroleum combustion, contamination from historical industrial activities, rail yards and transport corridors and fall-out from metal smelting practices. Like most countries in the world, smelting has caused heavy metal contamination in many urban areas of Australia (Oliver et al., 1999). Human health effects have been associated with elevated soil Pb levels, particularly in children, either due to direct consumption or transportation as finer particulates into the home as soil dust. Typically, regular hand to mouth behaviour occurs when the child is less than 6 years of age, and most prominent when < 2 (Lanphear, 2005). Estimates of soil ingestion and therefore soil contaminants are based on incidental ingestion associated with small particle size fractions. However, children are well known to consume large quantities of soil when they are young, which has raised some concern over acute toxicity and the accuracy of metal intake estimates via soil ingestion. This study investigated Pb bioaccessibility in 4 different particle size fractions (PSFs).

MATERIALS AND METHODS

The long-term contaminated soils (n = 18) had been contaminated principally from Cu or Pb/Zn smelters, although one soil sample was collected from a shooting range. Soils were also sampled approximately 20 km away the emission source. Sampled soils were passed through a 2-mm stainless steel sieve after air-drying and stored in clean plastic containers awaiting analysis. Material remaining in the sieve was gently pressed and rubbed to break any coarse aggregates. From, the 2-mm fraction, the <1000 µm, <250 µm and < 53 µm were subsequently sieved through stainless steel sieves. *In vitro* Pb bioaccessibility was estimated for each particle size fraction by the solubility bioaccessibility research consortium in vitro assay (SBRC), also known as the relative bioavailability leaching procedure (RBALP) (Kelley et al., 2002, Juhasz et al., 2009).

RESULTS

Bioaccessible Pb showed similar trends between PSFs as *aqua regia* digestions. Bioaccessible Pb generally decreased in the <1000 and <2000 µm particle size fractions relative to <250 µm, while the <53 µm fraction was markedly higher than the coarser fractions. Calculated enrichment ratios between fractions relative to the <2000 µm for the <53, <250 and <1000 µm in SBET ranged from 1.77-8.95, 0.88-125 and 0.63-1.65, respectively. Figure 1 shows the relationship between bioaccessible Pb in the < 2000 PSF and the <53, <250 and <1000 PSFs. The enrichment ratios for the full data set for the <53, <250 and <1000 were 3.63, 1.40 and 1.06, respectively.

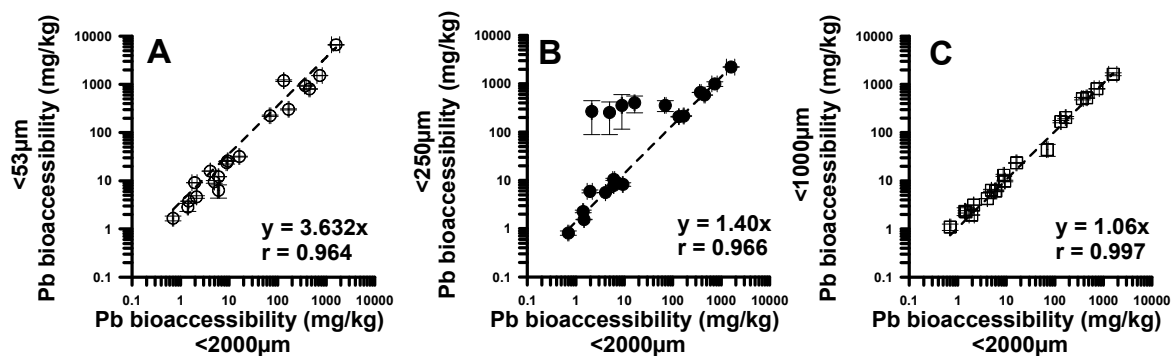


Figure 1. Enrichment of bioaccessible Pb in the <53 (A), <250 (B) and <1000µm (C) particle size fractions compared to the < 2000µm particle size fraction

Pb concentration was typically concentrated within the finer PSFs. However, in some sites large metal rich particles caused higher concentrations in the <2000 PSF. Bioaccessibility also appeared to be partly dependent on the concentration of soil Pb. A highly significant difference was observed in % Bioaccessibility between soils <50 mg Pb/kg and > 50 mg Pb/kg ($P < 0.0001$). However, there were no significant statistical interactions between PSFs and soil concentration. The bioaccessibility of Pb increased with decreasing PSF. Therefore, soil-Pb associated with dust and hands is highly bioaccessible. These observations demonstrate that not only is the total metal concentration in soil consumed during a pica episode likely to be lower relative to the PSFs <250 µm, but also that the proportion of Pb able to be extracted whilst in the stomach (<1 hr) is substantially lower. This indicates that total metal/kg concentrations in any fraction are often large overestimates of bioaccessible Pb. Given the low pH of the simulated fasting stomach environment, total concentrations in the 2-mm fractions are generally over-estimates of Pb bioaccessibility during soil pica events. In situations where exposure of children to Pb contaminated soil may exist in the future, the possibility of acute toxicity from childhood geophagy should be considered more cautiously due to high quantities consumed by children.

CONCLUSIONS

Data showed that Pb bioaccessibility was proportionally lower in the < 2000 µm compared to finer fractions. However, significant differences was only observed between the <53 and <2000 µm PSFs. Bioaccessibility of Pb in the finer particle size fractions was strongly and consistently related to bioaccessibility in the < 2000 µm fraction. Due to the strong relationship between Pb bioaccessibility of different particle size fractions, the use of coarser particle size fractions than <250 µm may be justified, avoiding time-intensive sieving.

REFERENCES

- JUHASZ, A. L., WEBER, J., SMITH, E., NAIDU, R., MARSCHNER, B., REES, M., ROFE, A., KUCHEL, T. & SANSOM, L. 2009. Evaluation of SBRC-gastric and SBRC-intestinal methods for the prediction of in vivo relative lead bioavailability in contaminated soils. *Environmental Science & Technology*, 43, 4503-4509.
- KELLEY, M. E., BRAUNING, S. E., SCHOOF, R. A. & RUBY, M. 2002. *Assessing oral bioavailability of metals in soils*, Columbus, Battelle Press.
- LANPHEAR, B. P. 2005. Childhood lead poisoning prevention. *JAMA: the journal of the American Medical Association*, 293, 2274.
- OLIVER, D., MCLAUGHLIN, M., NAIDU, R., SMITH, L., MAYNARD, E. & CALDER, I. 1999. Measuring Pb bioavailability from household dusts using an in vitro model. *Environmental Science & Technology*, 33, 4434-4439.

BIOREMEDIATION OF OIL CONTAMINATED SOIL BY DEGRADING BACTERIA AND ARBUSCULAR MYCORRHIZAL FUNGI

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INTRODUCTION

The use of micro-organisms and plants for bioremediation of PAH-contaminated environments seems to be a viable technology for restoration of polluted sites. Many bacterial strains have been isolated for their ability to transform, degrade and utilize PAHs as a source of carbon and energy (Mrozik et al., 2003). The role of mycorrhiza in phyto remediation has mainly focused on plant tolerance towards heavy metals and establishment of vegetation on polluted sites to prevent erosion. Yet, the widespread occurrence of mycorrhizas, their key role in plant stress tolerance and their impact on other microbial interactions in the rhizosphere have led to speculations on their possible involvement in new applications like degradation of organic pollutants through phytoremediation. The objective of this study was to determine the potential indigenous oil degrading bacteria and Arbuscular Mycorrhizal AM inoculation to remediate soils containing crude oil.

METHODS

400 Kg soil was collected from the surface (0-20 cm) of a pastoral location without a history of soil contamination. The soil was sterilized at 15 PSI and then deliberately contaminated with crude oil in a 1 and 2 wt% rate and incubated at room temperature for 4 weeks. Four treatments including plant multiflorum (T₁), plant multiflorum with mycorrhiza (Arbescolar-vezicular) inoculation (T₂), plant multiflorum with oil degrading bacteria inoculation (T₃), plant multiflorum with mycorrhiza and oil degrading bacteria inoculation (T₄) were applied. The bacteria used in the survey were indigenous degrading bacteria isolated from contaminated soil that belong to Staphylococcus, Acinetobacter and Pseudomonas genus.. 5 kg of oil-contaminated soil and uncontaminated soil were transferred to containers. Then 10 seeds of alfalfa (Medicago Sativa) were planted. After 8 weeks, shoots and roots were harvested separately to determine dry mass of root and shoots. The proportion of total root length colonized by the AM fungus was assessed. Petroleum hydrocarbon-contents in the soil samples were also extracted by soxhlet using a 1:1 (v/v) dichloromethane and n-hexane, and after purification analysed by Gas Chromatography.

RESULTS AND DISCUSSION

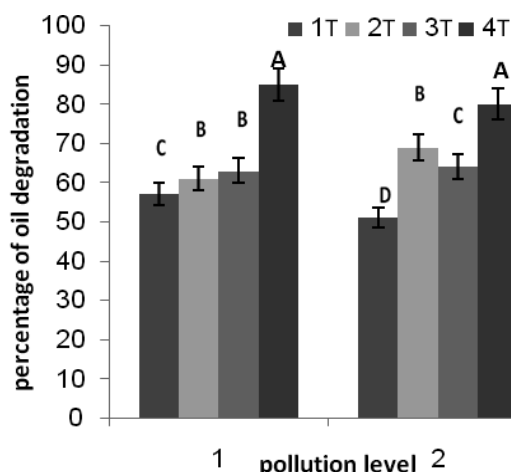
The shoot yield in uncontaminated soil was higher than those with 1% and 2% pollution levels and there was a significant difference in all treatments (Table 1). For example unpolluted soil's yield in mycorrhizal treatments was 1.8 and 2.7 fold greater than similar treatments yield in soils with 1% and 2% pollution levels respectively. In polluted soils due to the toxic effect of hydrocarbon compounds on plant growth, the yield was low and increasing in crude oil doses produced lower plant yields. Oil-degrading bacteria cause decomposition of these compounds probably, by releasing the biosurfactants and consequently led to increase the pollutant solubility. Mycorrhiza, by increasing in the absorbent organs volume and root adsorption efficiency via colonization mechanism, cause to increase in nutrient uptake by plant in one hand, and motivation the oil-degrading bacteria activity by preparing suitable media to increase the amount of oil compound decomposition. In fact by pollutant entry and causing stress, the amount of mycorrhiza due to it's positive role to enhance the plant resistance and nutrient uptake would increase and consequently cause colonization enhancement (Joner et al., 2006). The comparison between the treatments for both levels of pollution resulted in no significant difference between treatments efficiency except for forth one (inoculation of both mycorrhiza and oil-degrading bacteria). The amount of oil compound

decomposition in all treatments and both pollution levels were significantly ($P \leq 0.05$) difference compare to the soil control (Fig. 1). Among the all treatments, the one which received mycorrhiza and oil-degrading bacteria had the maximum efficiency to remove all those compounds. For example the amounts of decomposition for $C_{17}-C_{21}$, $C_{22}-C_{25}$, $C_{26}-C_{29}$ and $C_{30}-C_{36}$ were 72%, 63%, 75% and 75% respectively, while the amount of decomposition for such compounds in treatment including plant cultivation with pollution level of 1% and 2% were 46, 50, 12.5, and 12.5, respectively. The results of the present study indicated that the use of mycorrhiza fungi and bacteria played an important role in the bioremediation of oil-contaminated soil.

Table 1. Mean shoot and root dry matter yield and proportion of root length colonized by the AM fungus in oil-contaminated soil (mean \pm SE, n=3)

%pollution	Treatment	Shoot weight (g)	Root weight (g)	Mycorrhizal colonization (%)
0%	T1	29 \pm 1b	3.8 \pm .3b	0
	T2	36.9 \pm .9a	4.1 \pm .5a	43 \pm 1.8b
	T3	28.9 \pm .8b	3.76 \pm .2b	0
	T4	37 \pm 1.2a	4.2 \pm .7a	43 \pm 2.1b
1%	T1	9.5 \pm 1.1f	1.6 \pm .2d	0b
	T2	16.5 \pm .8d	2.75 \pm .3c	44 \pm .8b
	T3	15.9 \pm .9d	2.1 \pm .4d	0
	T4	23.6 \pm 1.3c	3.6 \pm .3b	46 \pm 1.1ab
2%	T1	2.1 \pm .3h	1.1 \pm .2e	0
	T2	10.3 \pm .8f	2.2 \pm .2d	42 \pm 2b
	T3	5.3 \pm .5g	2 \pm .1d	0
	T4	13.5 \pm 1.1e	3.25 \pm .3c	48 \pm 2.1a

Fig. 1. Effect of Bioremediation on total oil hydrocarbon degradation in the oil-contaminated soil



CONCLUSIONS

The result of this study offer that inoculation contaminated soil with mycorrhiza and degrading bacteria can be useful in remediation oil-contaminated soil.

REFERENCES

- Joner, E.J., Leyval, C., Colpaert, J.V., 2006. Ectomycorrhizas impede phytoremediation of polycyclic aromatic hydrocarbons (PAHs) both within and beyond the rhizosphere. *Envir. Sci. & Tech.* 142(1), 34–38.
- Mrozik, A., Piotrowska-Seget, Z., Łabu_ek, S., 2003. Bacterial degradation and bioremediation of polycyclic aromatic hydrocarbons. *Polish J. of Envir. Stu.* 12(1), 15–25.

THREE STAGE REDUCTION OF PHENOLS IN WASTEWATER: CHEMICAL, OZONE AND BACTERIAL TREATMENT

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INTRODUCTION

The wastewater used in this trial was produced during the processing of coke from coking coal. During this process, coal/coke requires quenching with water, where the quench water is sprayed and directly contacts the coke/coal. The water is collected in a collection pit and pumped into a tank before being reused again for quench water. The quenching water dissolves many carbon compounds into the water, of which phenols are a component. Due to the OH&S concerns with human exposure to phenols, the phenols have to be reduced/removed from the quench water before reuse. The aim of the trial was to identify and quantify the reduction in phenols that can be achieved with using a three stage treatment process utilising chemical treatment, oxidation with ozone and degradation with SAS Water Solutions' bacteria product ComBact, specifically designed for phenol reduction.

METHODS

A three stage treatment process was investigated with the aim of reducing phenols:

1. Chemical treatment to remove the TSS containing phenols
2. Oxidation of phenols with ozone;
3. Degradation of the remaining phenols with bacteria product ComBact.

Stage 1

The first stage chemical treatment was introduced after the phenol loading was found to be too high for stages 2 & 3 to provide sufficient reduction. This was due to the very high total suspended solid (TSS) loading, which contained phenols. Samples of untreated quench water were treated with an organic coagulant (500 mg/L) and the pH adjusted to 7.5 to precipitate TSS. The water was then sampled and submitted to the laboratory for analysis.

Stage 2

The second stage of the trial was conducted on-site. The water was treated utilising ozone generating equipment and a reaction tank. Water was gravity fed from the storage tank through a reaction tank into which the ozone was diffused. After oxidation was complete, the water was then returned to the collection pit before being recycled for reuse. The water was set to a constant flow rate and constant ozone rate. The water was then sampled and submitted to the laboratory for analysis.

Stage 3

The third stage involved the addition of 40 g/L of phenol reducing bacteria into the ozone treated water with aeration. The bacteria are SAS Water Solutions' ComBact range, which have been specifically selected for phenol reduction. After 36 hours the water was again sampled and submitted to the laboratory for analysis.

RESULTS AND DISCUSSION

Untreated Quench Water

The untreated quench water was tested for phenol content on three days and total organic carbon (TOC) on one day. The results were as follows:

Table 1. Untreated quench water phenols & total organic carbon (TOC) concentrations.

Date	Phenols (mg/L)	TOC (mg/L)
11-10-2010	2,400	12,220
13-01-2011	4,620	
11-05-2011	4,015	

The results in Table 1 show that there are substantial concentrations of phenols in the quench water. The phenols concentration varies significantly in the three samples. This variation is related to the number of times the water has been recycled for quenching.

Treated Water – Initial Testing

Table 2 below shows the reduction in phenols achieved from initial testing, which only utilised stage two and three treatment process (ozone and bacteria).

Table 2. Treated quench water phenols concentrations (initial testing).

Date	Untreated Quench Water (mg/L)	Ozone Treated Water (mg/L)	Bacteria Treated Water (mg/L)
13-01-2011	4,620	2,830	1,700

At a constant flow rate of 356 L/hour the ozone unit oxidised the phenols in the quench water by approximately 39%, from 4,630 to 2,830 mg/L. This is a significant reduction in the phenols and confirms that ozone oxidation of phenols is a viable treatment option. The ozone dose was 50 g/hour.

ComBact bacteria reduced the phenols concentration in the primary treated quench water from 2,830 to 1,700 mg/L (40% reduction). This significant reduction confirms ComBact as a potential treatment option, which requires further investigation. The ComBact bacteria are recommended to be used in water in which the concentration of phenols is less than 2,000 mg/L. In this case the phenols concentration in ozone treated quench water was unknown when the bench-scale trial commenced, and was actually above the recommended limit. The results may be improved with a lower initial phenols concentration. Further testing was conducted which included a primary chemical treatment stage.

Treated Water – Further Testing

The primary stage treatment removed precipitated solids at pH 7.5 after dosing with an organic coagulant. This treatment reduced the phenol component from 4015 mg/L to 3270 mg/L (19% reduction) for improved subsequent ozone and bacteria treatment. The treated wash water enters a settling tank to separate the sludge from the cleaner wash water. The colour was less intense and the odour was reduced slightly at this pH. The precipitated sludge dewatered easily and can be left to dry in a filter bag setup.

Bacteria treatment is highly selective and efficient for reducing phenolic compounds. Under oxidising conditions the bacteria catalyses the phenol compounds to form free radicals, which undergo spontaneous polymerisation. The polymerised product precipitates out of the solution where oligomers and polymers are produced, which are less toxic than phenols.

CONCLUSIONS

Based on the above chemical, ozonation and bacterial treatment performance in reducing phenols, it is expected that the offensive odours caused by the by-products of the quenching process will be successfully reduced. The strong phenolic smell was almost instantly reduced in the presence of the bacterial product.

Based on the bench-scale tests, and when combined with the current ozone treatment on-site, the final phenol levels are predicted to be <1000 mg/L. These trials are ongoing.

IMMOBILIZATION OF COPPER IN COPPER MINE SOIL USING BIOSOLIDS-BASED CO-COMPOSTED PRODUCTS

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INTRODUCTION

Soil pollution by heavy metals is a global environmental problem because although heavy metals are generally persistent in nature they can also become mobile. A fraction of their total mass in soil becomes bioavailable to plants and animals, or leaches to groundwater that may harm the environment. Remediation of metal contaminated soils generally involves the removal of metals, which is an expensive process. A low cost technology to remediate heavy metal polluted soils is the addition of soil amendments *in situ*. This can favour chemical immobilization by reducing the mobility and bioavailability of metals through precipitation or adsorption (Santona *et al.*, 2006; Park *et al.*, 2010). Biosolids-based co-composted products can be used as an effective sink for reducing the bioavailability of metals in contaminated soils (Theodoratos *et al.*, 2000; Bolan and Duraisamy, 2003; Brown *et al.*, 2003). The aim of this study was to assess the ability of biosolids alone and, biosolids blended with lime, red mud, fly ash and bentonite to reduce the mobility of heavy metals in contaminated soil. The effects of soil pH and dissolve organic carbon (DOC) on the redistribution of Cu was investigated using a Cu mine soil in order to better understand: firstly, the mechanism responsible for metal fixation; and secondly, changes in the Cu redistribution as affected by different amendments.

METHODS

The biosolids sample was collected from the Bolivar Wastewater Treatment Plant in South Australia. It was air dried and sieved to < 2 mm using a stainless steel sieve and then mixed with lime at 5% w/w basis and red mud, coal fly ash and bentonite at 20% w/w basis. All samples were wetted to 70% of the water holding capacity (WHC) and were incubated under aerobic conditions at room temperature in plastic bags. The samples were incubated for three months before applying to tested soil. Surface samples (0-20 cm depth) of naturally contaminated mine soil with elevated residual concentration of Cu (36100 mg kg⁻¹) was collected from an abandoned Cu mine at Kapunda, South Australia. Soils were air-dried and sieved (< 2 mm) and then mixed in a concrete mixer. The soil sample was mixed with biosolids alone, biosolids blended with lime, red mud, fly ash and bentonite at 10% w/w basis (i.e. 50 Mg ha⁻¹). All samples were wetted to 70% of the WHC and incubated under aerobic condition for 5 months in a controlled room at 25°C. All treatments were in triplicate and the container weight was monitored once a week. When the soil incubation study was completed, soil samples in containers were taken and air-dried at 30°C and then analyzed for pH, DOC, NH₄NO₃ extractable Cu (Cu_{NN}) and Cu concentrations in the sequential extraction using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Agilent.

RESULTS AND DISCUSSION

At the end of the incubation period, the amendments mixed with Cu mine soil increased the DOC and pH value and it was higher than the control soil. Soil samples treated with biosolids alone increased DOC concentration higher than the other amendments while the Cu mine soil mixed with biosolids blended with lime and red mud increased soil pH above that of the other amendments.

At the end of the incubation period, all amendments when mixed with Cu mine soil reduced the concentration of Cu_{NN} and it was lower than the control soil (Fig. 1A). For example, the concentration of Cu_{NN} of Cu mine soil alone was $10724.9 \text{ mg kg}^{-1}$ while Cu mine soil treated with biosolids mixed with lime reduced Cu_{NN} concentration to a level lower than the other amendments and was $5670.0 \text{ mg kg}^{-1}$. All amendment applications increased organically bound, carbonate and Mn/Fe oxyhydroxide bound of Cu fractions (Fig. 1B). Application of biosolids blended with lime increased the percentage of carbonate bound of Cu in mine soil more than the other biosolids-based co-composted products. Biosolids blended with red mud increased the percentage of Mn/Fe oxyhydroxide bound of Cu in mine soil more than biosolids alone and biosolids blended with lime, fly ash and bentonite.

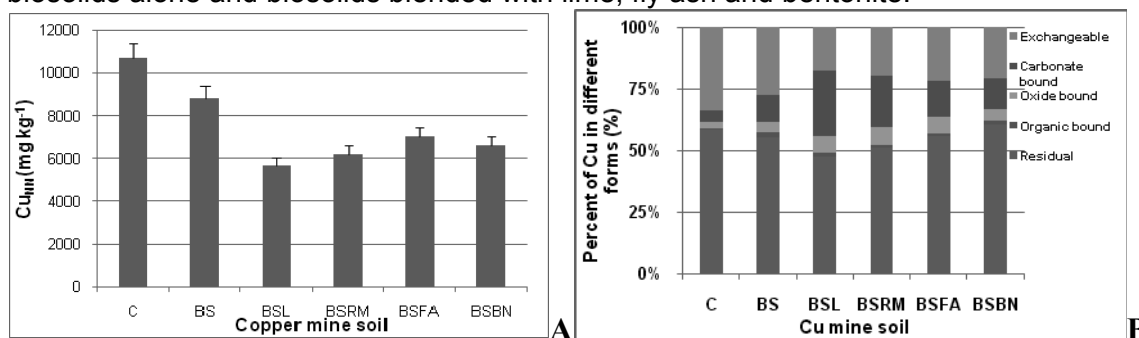


Fig.1 (A) The Cu_{NN} concentration and (B) the percentage of Cu in different forms in Cu mine soil (C; control) treated with biosolids alone (BS) and biosolids blended with lime (BSL), red mud (BSRM), fly ash (BSFA) and bentonite (BSBN) at the end of the incubation period. Error bars indicate the standard deviation between replicates.

CONCLUSIONS

The co-composting of biosolids with lime, red mud, fly ash and bentonite can be used as an effective sink for reducing the bioavailability of Cu. These co-composted products are more beneficial than biosolids alone when applied to Cu mine soil. Biosolids blended with lime was the most effective in the immobilization of Cu in mine soils as measured Cu_{NN} concentration. However, some studies have shown that organic amendments can actually increase metal availability in the long-term due to organic-complexation (Ruttens *et al.*, 2006). Long-term stability and biogeochemical techniques of metal(loid)s immobilization by organic amendments should be investigated, and long-term stabilizing techniques development.

REFERENCES

- Bolan, N.S. and Duraisamy, V.P. (2003). Role of inorganic and organic soil amendments on immobilization and phytoavailability of heavy metals: a review involving specific case studies. *Australian Journal Soil Research*. **41**, 533-555.
- Brown, S.L., Henry, C.L., Chaney, R., Compton, H. and DeVolder, P.S. (2003). Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. *Plant and Soil*. **249**, 203-215.
- Santona, L., Castaldi, P. and Melis, P. (2006). Evaluation of the interaction mechanisms between red muds and heavy metals. *Journal of Hazardous Materials*. **136**, 324-329.
- Ruttens, A., Colpaert, J.V., Mench, M., Boisson, J., Carleer, J. and Vangronsveld, J. (2006). Phytostabilization of a metal contaminated sandy soil. II: Influence of compost and/or inorganic metal leaching. *Environmental Pollution*. **144**, 533-539.
- Theodoratos, P., Moirou, A., Xenidis, A. and Paspaliaris, I. (2000). The use of municipal sewage sludge for the stabilization of soil contaminated by mining activities. *Journal of Hazardous Materials*. **77**, 177-191.

COMPARATIVE EFFECTS OF COMPOST AND INORGANIC FERTILIZER ON LEAD TRANSPORT AND ACCUMULATION IN MAIZE CROP GROWN ON HEAVY METAL CONTAMINATED SOIL IN NIGERIA

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INTRODUCTION

The hazard associated with heavy metal contamination of the agricultural land eventually ends up with human being through food chain. Heavy metals are said to enter into animals and human beings through ingestion of contaminated plants/crops (CDC, 1991). Toxic levels of lead (Pb) in cultivated crops have been reported (Pallavi and Dubey, 2005). The concern of Crop Physiologists however, is in reducing the heavy metal accumulation in plant grown on contaminated soil so as to prevent plant and animal toxicity.

Heavy metal accumulation in plant depends on its concentration and availability in the soil. Organic ammendment is effective in reducing the concentrations of heavy metals in contaminated sites through transformation and immobilization (Bolan *et al.*, 2010). It modifies plant nutrition by supplying the plants with more of essential elements. Effectiveness of two types of compost and inorganic fertilizer on the lead (Pb) uptake by maize crop at different stages of development on battery waste contaminated site was assessed in Ibadan, Nigeria.

METHODS

The experiment was conducted on the defunct Exide battery waste dump-site at Ori-Ile, Kumapayi of Egbeda Local Government Area in Ibadan, Oyo State, Nigeria.

Compost Preparation and experimental procedure

Composts were prepared by mixing Mexican sunflower (MSC) and cassava peels (CPC) separately with poultry manure in ratio 3:1 and composted for 12weeks. Both were applied at the rates of 0, 20 and 40t/ha while inorganic fertilizer (NPK, 20:10:10) was applied at 100kgN/ha. The treatments were MSC40, MSC20, CPC40, CPC20, F1 and Control (0t/ha). The plot size was 4 x 3m and experimental design was Randomized Complete Block with four replications. Composts were applied one month before planting. Maize plants were randomly selected and uprooted from each treatment at one, two and three month(s) after planting (i.e 1MAP, 2MAP and 3MAP) for chemical analysis. The uprooted plants were separated into different parts (i.e root and shoot) oven-dried to a constant weight at 80°C, milled and representative samples taken for the determination of Pb concentrations in the plant tissue. Available Pb concentrations in the soil samples taken at 0 – 15cm depth before and after cropping were determined using the method described by Smejkalova *et al.* (2003). Data were analysed using ANOVA and means separated by Duncan Multiple Range Test (DMRT).

RESULTS AND DISCUSSION

Lead concentration (138000mg/kg) was abnormally high in the soil at the study site. The Pb concentration was reduced in all the compost treated plants and the highest recorded in the inorganic fertilizer treatment followed by control. This was as a result of Pb precipitation in the compost-amended soil to insoluble complexes in the presence of nutrient ions like Calcium and Phosphate (Bolan *et al.*, 2010) thereby reducing Pb bioavailability. In the maize

stems and leaves, the concentrations at 1MAP were higher than at 2MAP in all the treatments ($P < 0.05$) probably due to formation of complexes and sequestration of Pb in cellular structure like vacuole (Seregin *et al.*, 2004) while there was no significant reduction in the root. The highest concentration of Pb in all the treatments was found in the root throughout the sampling periods. Compost enhanced maize growth by improving soil conditions while the plants in control and inorganic fertilizer treatments, were stunted, chlorotic, with dark and scanty roots. They later withered and died. Remarkable reduction in the leaf Pb concentration was also observed in compost-treated plants at 3MAP compared to other sampling periods except in MSC40 (Table 1). The high Pb concentrations in maize tissues (above the EU permissible level of 0.03 mg/kg) agrees with the report of Miller and Koepe (1970).

Table 1. Total Pb concentration (mg/kg) in the maize plant parts at different sampling periods

Treatments	Leaf 1MAP	Stem 1MAP	Root	Leaf 2MAP	Stem 2MAP	Root	Leaf 3MAP	Stem 3MAP	Root
Control	11800 ^a	6790 ^c	17000 ^a	6810 ^a	6920 ^b	15900 ^a	NA	NA	NA
MSC20	8790 ^b	3680 ^d	9670 ^b	591 ^b	562 ^c	9060 ^b	165 ^{ab}	178 ^{cd}	11200 ^{ab}
MSC40	8390 ^b	8410 ^{ab}	9940 ^b	472 ^b	474 ^c	9270 ^b	530 ^a	334 ^{bc}	13400 ^a
CPC20	9130 ^{ab}	7560 ^{bc}	9750 ^b	992 ^b	809 ^c	11000 ^b	204 ^{ab}	430 ^b	11400 ^{ab}
CPC40	9090 ^{ab}	3720 ^d	9610 ^b	3420 ^a	524 ^c	11600 ^b	182 ^{ab}	1179 ^a	8700 ^b
F1	12000 ^a	9070 ^a	17900 ^a	6200 ^a	7930 ^a	15900 ^a	NA	NA	NA

Means followed by the same letter in a column are not significantly different from each other ($P < 0.05$). NA= Not Available

CONCLUSIONS

Compost amendment reduced total Pb accumulation in maize plant parts.

REFERENCES

- Centre for Disease Control. 1991. Preventing lead poisoning in young children. U.S. Department of Health and Human service Atlantic GA. Public Health service centres for disease control.
- Pallavi Sharma, Rama Shanke Dubey. 2005. Lead toxicity in plants. *Brazillan journal of plant physiology* vol 17.No 1 Print ISSN 1677-2420.
- Seregin I.V., Shpigur L.K., Ivaniov V.B. 2004. Distribution and toxic effects of Cd and Pb on maize roots. *Russ. J. plant physiology*. 51:525-533
- Smejikalova M., Milkanova O. Boruvka L. 2003. Effects of heavy metal concentrations on biological activity of soil micro-organisms. *Plants environ* 7:321-326.
- 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. No 3 (2010) pp 1-18
- Miller R.J. and Koepe D.E. 1970. Accumulation and physiological effects of lead in corn. *Proc., 4th Ann. Conference Trace substances Environ. Health*. University of Missouri, Colombia.

CARBON INPUT BY LITTERFALL AND SOIL RESPIRATION OF A RED PINE STAND WITH VARYING DEGREE OF DAMAGE FROM PINE WILT DISEASE

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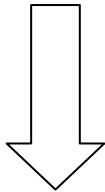
INTRODUCTION

Pine wilt disease caused by the pine wood nematode (*Bursaphelenchus xylophilus*) has become a serious threat to Korean pine ecosystems (Shin and Han 2006). Additionally, forest insects and disease can have large effects on the carbon (C) cycles by killing or damaging trees (Morehouse et al. 2008). The change of C dynamics following the pine wilt disease incidence has received little research attention, although this represents a major forest disaster in pine forest ecosystems of Korea. The objectives of this study were formulated to quantify the impacts of pine wilt disease on soil respiration and C inputs of litterfall at various levels of damage intensities of pine wilt disease in red pine stands.

METHODS

The study site was located in Jinju City, which is the most severely damaged pine wilt disease area in Korea since the disease outbreak in 1998. Nine plots having various damage intensities of pine wilt disease were established on the same facing slopes and aspects (Table 1). Litter was collected seven times between 29 May 2009 and 20 May 2010. Soil respiration rates were measured monthly *in situ* using an infrared gas analyzer system (Model EGM-4, PP systems, Hitchin, UK) during the same period.

Table 1. Stand characteristics at the study site

Damage intensity of pine wilt disease	Tree density (tree/ha)	Mean DBH (cm)	Basal area (m ² /ha)
 Slight	2,500	12.60 (8.0-18.9)*	33.07
	2,100	14.08 (6.0-21.5)	35.88
	1,800	15.40 (9.5-21.0)	35.45
	1,500	14.22 (8.1-19.3)	25.25
	1,300	16.36 (11.0-23.0)	28.57
	1,100	12.56 (9.7-17.0)	14.30
	800	14.54 (11.2-21.6)	13.93
	500	15.36 (10.8-19.9)	9.70
	Severe	300	13.23 (12.0-14.4)

DBH, diameter at breast height. *Mean (range).

RESULTS AND DISCUSSION

The C inputs from litterfall decreased with increasing damage intensity from pine wilt disease due to a considerable difference in the stand basal area among the study plots (Fig. 1) because stand basal area is generally the major factor limiting litterfall amount in many temperate forest ecosystems (Kim et al. 2009). Correlation analysis results show a strong linear relationship ($P < 0.05$) between C inputs of the litter fall and basal area accounting for 62-84% of the variation, except for the C inputs from cone and flower litter (Fig. 1).

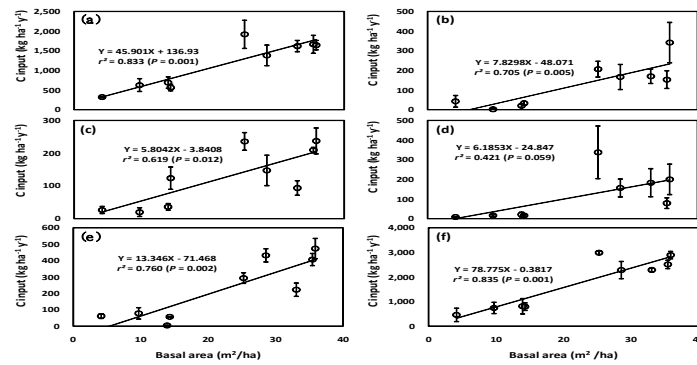


Fig. 1. Relationships between basal area and carbon (C) inputs in litterfall components (needles in the fall season [a], needles in the spring season [b], branches [c], bark [d], cones and flowers [e], miscellaneous [f]) in pine wilt disease stands.

Mean annual soil respiration rates ($0.39 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ / $0.27 - 0.52 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$) showed the second-order polynomial relationships with basal area in pine wilt disease stands (Fig. 2). This result could be attributed to the change in environmental conditions (e.g. soil temperature) for microbial or root growth activity and organic matter decomposition and/or the decrease in root respiration after removing of the infected trees. Soil temperature with high basal area stands was lower than that with medium or low basal area stands for the growing season. Decreased soil respiration rates in low basal area stands could be due to decreased root respiration.

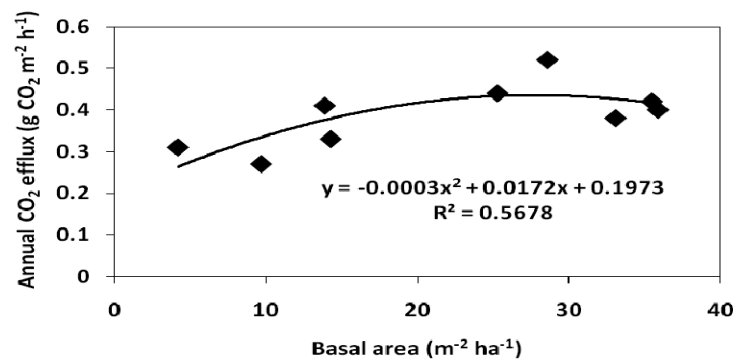


Fig. 2. Relationship between soil respiration and stand basal area at various levels of damage intensities in pine wilt disease stands

CONCLUSIONS

The damage intensity of pine wilt disease greatly altered the quantity of C by litterfall components and soil respiration in a natural pine stand. The results indicate that pine wilt disease is likely to have an impact to C cycles by litterfall and soil respiration, thus the cycles could be differed considerably among damage intensities of pine wilt disease stands.

REFERENCES

- Kim, C., Son, Y., Lee, W.K., Jeong, J., Noh, N.J. (2009) Influences of forest tending works on carbon distribution and cycling in a *Pinus densiflora* S. et Z. stand in Korea. *For Ecol Manage* 257: 1420-1426.
- Morehouse, K., Johns, T., Kaye, J. and Kaye, M. (2008) Carbon and nitrogen cycling immediately following bark beetle outbreaks in southwestern ponderosa pine forests. *For Ecol Manage* 255: 2698-2708.
- Shin, S.C., Han, H.R. (2006) Current status on research and management of pine wilt disease in Korea. *International Symposium of Current Status on Research & Management of Pine Wilt Disease*, 2006 Oct 20, Seoul, pp 31-44.

NITROUS OXIDE EMISSION FROM ORGANIC AMENDMENTS

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INTRODUCTION

The second largest source of Australia's national inventory of greenhouse gas (GHG) emissions is agricultural sector comprising emissions mainly from livestock enteric fermentation, manure management, organic and inorganic fertiliser application, rice cultivation, and savannah and field burning of agricultural residues (NGGI, 2009). Nitrous oxide (N₂O), a potential and a major GHG from agricultural activities is released as an intermediate compound from the microbial transformations of nitrogen (N) in soils.

Large quantities of organic amendments such as biosolids, poultry and pig manure and farmyard compost are added to soils to improve the physical, chemical and biological fertility of soils. For example, in Australia approximately 220,000 dry tonnes of biosolids are produced annually, with 48% applied to agricultural land and the remainder is used in forestry, landfill and composting. The use of organic amendments in agriculture holds dual benefits for the waste producing industries by providing a primary avenue for safe and beneficial recycling of these resource materials and for the primary producers by providing an alternative source of nutrients and soil conditioning properties. Besides many benefits, these resources may also contain toxic heavy metals and enteric pathogens, and also may lead to GHG emission (Lal et al., 2002; Bolan et al., 2004).

Application of nitrification inhibitors (NIs) and urease inhibitors (UIs) are proved to be one of the best practices to reduce N losses including N₂O emission from soils. The objectives of this project are: (i) to compare N₂O emission between organic and inorganic N sources and (ii) to examine the effect of urease and nitrification inhibitors on N₂O emission.

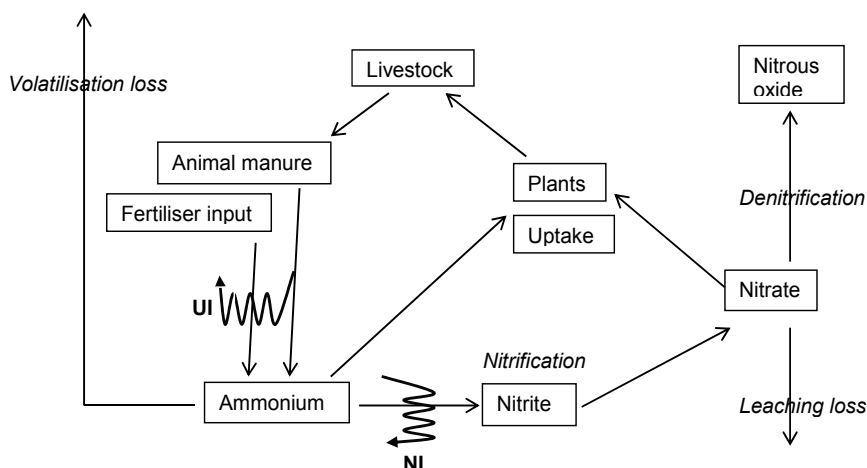


Figure 1. N cycle depicting N loss pathways in soils and the role of urease (UI) and nitrification (NI) inhibitors in controlling N transformation.

SOIL NITROUS OXIDE EMISSION PROCESS

In soils, N transformation occurs through various microbial processes that include:

- Mineralisation involving amination and ammonification. Amination is a microbial process of hydrolysing macromolecules of organic N compounds (proteins) into simpler N compounds (amines & amino acids). Ammonification, a microbial process in which amines and amino acids are converted to ammonium ions.

- Nitrification, a two-step microbial process of oxidising ammonium ions into nitrite and then into nitrate ions.
- Denitrification, anaerobic reduction process in which nitrate ions are converted to nitrogen gases and released into the atmosphere.

N₂O production can occur from both incomplete nitrification and denitrification processes. The rate of N₂O emission can be influenced by the source and level of N input, climate (temperature, rainfall), soil texture, soil organic C, soil pH, crop type and management practices like tillage, irrigation and drainage.

N₂O mitigation strategies

Many approaches have been used to mitigate economic and environmental impacts of N losses. Best management practices that increase crop uptake of N directly (e.g. source of N input, application timing, application method, matching of N supply with crop demand) and use of inhibitors (UIs and NIs) play a major role in mitigating N loss as N₂O into the atmosphere. UIs delay the conversion of urea to ammonium by inhibiting Urease enzyme thereby reducing the potential of ammonium volatilisation from the soils and availability of substrate for nitrification. NIs reduce the rate at which ammonium is converted to nitrate by interfering with the metabolism of microorganisms involved in the conversion pathway. N- (n-butyl) thiophosphoric triamide, Agrotain and Nitrapyrin, Dicyandiamide (DCD) are some of the commonly used UIs and NIs in agriculture. Many research trials have confirmed the economic and environmental benefits of inhibitors in controlling N losses from fertiliser and animal excreta (Di & Cameron, 2003; Singh et al., 2008; Asing et al., 2008; Kelly et al. 2008).

CONCLUSIONS

Application of inhibitors has shown to be effective in reducing nitrous oxide emission from soils. However, the currently available research is limited in their application to agriculture and pasture lands where inorganic fertilisers (like urea) are the major sources of nitrous oxide production. Considerably, more research is required in this area to provide information on inhibitors' effects on agricultural soils treated with organic amendments in Australia.

REFERENCES

- Asing, J., Saggar, S., Singh, J. and Bolan, N.S. (2008) Assessment of nitrogen losses from urea and an organic manure with and without nitrification inhibitor, dicyandiamide, applied to lettuce under glasshouse conditions. *Aust. J. Soil Res.* 46: 535-541.
- Bolan, N.S., Adriano, D.C., Mahimairaja, S. (2004) Distribution and bioavailability of trace elements in livestock and poultry manure by-products. *Critical Rev. Environ. Sci. Tech.* 34: 291 – 338.
- Kelly, K., Phillips, F. and Baigent, R. (2008) Impact of dicyandiamide application on nitrous oxide emissions from urine patches in northern Victoria, Australia. *Aust. J. Exp. Agr.* 48: 156-159.
- Di, H.J. and Cameron, K.C. (2003) Mitigation of nitrous oxide emissions in spray-irrigated grazed grassland by treating the soil with dicyandiamide, a nitrification inhibitor. *Soil Use Mgmt.* 19: 284-290.
- Lal, R. (2002) The potential of soils of the tropics to sequester C and mitigate the greenhouse effect. *Adv. Agron.* 76: 1-30.
- NGGI (2009) National Greenhouse Gas Inventory- Kyoto Protocol Accounting Framework, Department of Climate Change and Energy Efficiency, Canberra, Australia.
- Seaker, E.M., Sopper, W.E. (1983) Reclamation of deep mine refuse banks with municipal sewage sludge. *Waste Manage. Res.* 1: 309-322.
- Singh, J., Saggar, S., Giltrap, D.L. and Bolan, N.S. (2008) Decomposition of dicyandiamide (DCD) in three contrasting soils and its effect on nitrous oxide emission, soil respiratory activity, and microbial biomass- an incubation study. *Aust. J. Soil Res.* 46: 517-525.

METAL TOLERANT PAH DEGRADING BACTERIA — PATTERNS OF METAL TOLERANCE AND ENVIRONMENTAL RELEVANCE

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INTRODUCTION

Mixed contaminated sites are the complex, multi-component system with a range of different organic and inorganic chemicals co-existing together under various physio chemical conditions (Thavamani et al., 2011). The sites contaminated with both organic xenobiotics and heavy metals represent a high percentage of the hazardous waste sites listed for remediation (Tremaroli et al., 2009). As such remediation of mixed contaminated sites is major challenge for remediators. Polycyclic aromatic hydrocarbons (PAHs) are compounds of intense public concern owing to their persistence in the environment and potential deleterious effects on human health. Microbial degradation has been proposed as an inexpensive and efficient method to remove PAHs. However PAHs mostly occur together with heavy metals at sites such as former manufactured gas plant sites, wood preservation sites, metallurgical industries, where heavy metals could interfere with PAH degradation process. Metal resistant PAH degrading bacteria is one of the viable strategies to mitigate metal inhibition of organic compound biodegradation. Determining bioavailable metal concentrations is a vital step in the process of standardizing experiments to determine the impact of metals on organic pollutant biodegradation. Solution phase metal concentration is considered to be most toxic and bioavailable. Many microbial growth media contain high concentrations of metal-binding components such as phosphates that can reduce solution-phase metal concentrations.

METHODS

In this study we isolated three novel PAHs degrading bacteria from long term mixed contaminated soils collected in Australia. Cadmium was chosen as a model heavy metal compound to test metal tolerance and PAH degrading ability using our optimized mineral medium. To achieve maximum bioavailable metal concentration (Cd^{2+}) in growth media we have developed an optimised mineral media (OMM). The bioavailable Cd concentration (Cd^{2+}) in the optimised mineral medium was modelled using VMINTEQ and confirmed by measuring with ion selective electrode (ISE).

RESULTS AND DISCUSSION

The developed optimised mineral medium had more than 60% Cd^{2+} concentration at pH 6.5. The Cd tolerance patterns of three isolates were tested using this medium. The pure culture *Achromobacter* sp. had the highest minimum inhibitory concentrations (MIC) of 7mg/L cadmium followed by consortium-5 (5mg/L) and consortium-9. The cadmium resistance and PAH degradation ability was tested in a model system consisting of 5 mg/L of Cd and 200 mg/L of phenanthrene. All the isolates were able to degrade phenanthrene completely in less than four days in the presence of Cd.

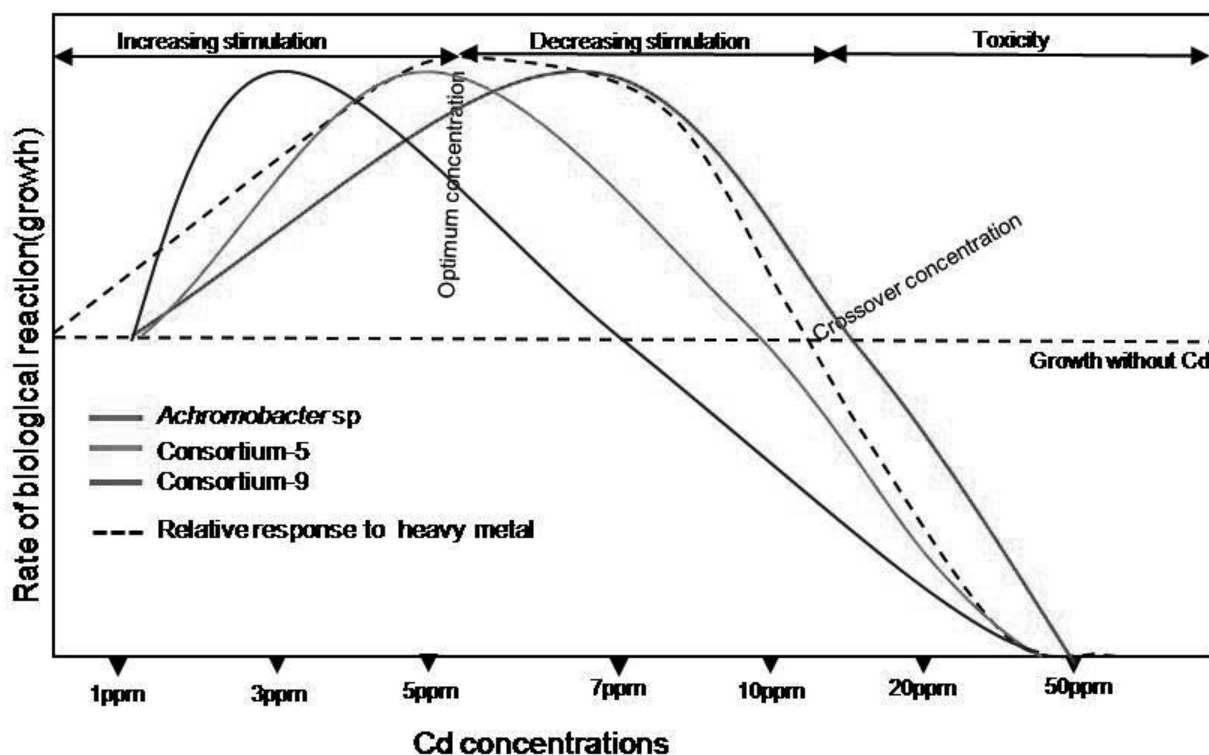


Fig.1.The relative response of bacterial strains to the presence of Cd demonstrated by modified McCarthy heavy metal toxicity curve.

CONCLUSIONS

All the three bacterial cultures exhibited different patterns of Cd tolerance. The *Achromobacter* sp. had highest Cd tolerance (MIC) followed by consortium-5 and consortium-9. The comparison of phenanthrene degradation in model system demonstrated the ability all the tested bacteria to degrade phenanthrene in the presence of cadmium. This study clearly suggests the potential of these bacteria to remediate sites contaminated with PAH and heavy metal mixtures.

REFERENCES

- Thavamani, P., Megharaj, M., McFarland, R., Naidu, R. (2011) Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: implications to bioremediation. *Environ Int* 37: 184-189.
- Tremaroli, V., Workentine, M.L., Harrison, J.J., Fedi S, Ceri, H, Turner RJ, Zannoni D. (2009) Metabolomics investigation of bacterial 1 response to metal challenge. *App Environ Microbiol*, 75: 719-28.

EFFECT OF RECYCLED WATER SOURCES ON THE BIOAVAILABILITY OF COPPER TO EARTHWORMS AND MICROORGANISMS

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INTRODUCTION

Farmers in many countries use recycled water for irrigation because it is a rich source of organic matter and essential plant nutrients. Copper (Cu) is an essential element that all organisms need; but at high concentrations, Cu has a detrimental effect on soil microorganisms and earthworms. Heavy metal bioaccumulation by earthworms and aberration of the microbial activities can serve as an ecological indicator of metal bioavailability in contaminated soils. (Naidu et al., 2008). Sources of anthropogenic Cu contamination include the application of pesticides, fertilizers, sewage sludge and recycled waters to land. Recycled water irrigation has also been shown to increase the amount of dissolved organic carbon (DOC) in soils either by acting as a source of DOC or by enhancing the solubilization of soil organic matter. The DOC has often been shown to influence the mobility and bioavailability of metal contaminants by forming soluble metal-DOC complexes (Bolan et al., 2011). In this study, bioavailability of Cu to earthworms as measured by mortality and avoidance test and effect of Cu on microbial activity as measured by respiration and microbial biomass carbon was examined at various levels of Cu in the presence of MQ water and recycled water sources.

METHODS

Earthworm toxicity and microbial activity experiments were undertaken using two soils (Gawler-sandy loam and Adelaide Hills-silt loam) varying in their texture, pH and organic matter content. The recycled sources used were farm dairy effluent (FDE), winery effluent (WE) and piggery effluent (PE). The two soils were spiked with different concentrations (0, 100, 500 and 1000 mg kg⁻¹) of Cu added as copper nitrate which were incubated for a week at field capacity. After a week, the Cu-amended soils were further incubated with recycled water sources or MQ-water (as a control) for 3 months (earthworm experiment) and 45 days (microbial activity experiment) at field capacity. Sub-samples of these soils were used for both the earthworm and microbial activity experiments. Earthworm avoidance test was performed using two and six-chamber test containers (Hund-Rinke et al., 2005). For the mortality experiment, 10 matured *Eisenia fetida* worms were weighed and added to each of the 3 replicates and cultured at 20 (±2) °C with continuous light. At the end of 2 weeks, the live earthworms were counted and their weights recorded. The earthworms were depurated for 24 h and digested with 5 ml of conc. HNO₃. The samples were diluted with MQ water and analysed for total Cu using ICP-OES. At the end of the mortality test the soil samples were analyzed for pH and CaCl₂ extractable free Cu²⁺. The microbial activity of Cu contaminated soils was examined by measuring: 1. Basal respiration (Bloem et al., 2006); 2. Substrate induced respiration (Anderson and Domsch, 1978); 3. Inhibition of substrate induced respiration (Anderson and Domsch, 1975); 4. Microbial biomass carbon (MBC) (Vance et al., 1987) and 5. Metabolic quotient (Anderson and Domsch, 1990).

RESULTS AND DISCUSSION

The results for the earthworm toxicity test indicated that the worms clearly avoided soils with high levels of Cu concentrations. Mortality of earthworms increased as Cu concentration increased. Recycled water sources decreased the accumulation of Cu in earthworms (Fig.

1a) and the metal concentration of earthworms was dependent on CaCl_2 -extractable free Cu^{2+} concentrations in the soil. In the microbial activity experiment, the results suggested that the effect of Cu on soil microbial activity as measured by various parameters varied between MQ water and recycled water sources which may be attributed to the difference in the concentration of DOC. Respiration rates, MBC and fungal: bacterial activity ratio decreased significantly as Cu concentration increased during the 45 d incubation period. Metabolic quotient values were lower in soils in the presence of recycled water than in the MQ water indicating that recycled water sources decreased the inhibitory effect of metals on microbial activity as measured by respiration and microbial biomass carbon (Fig. 1b).

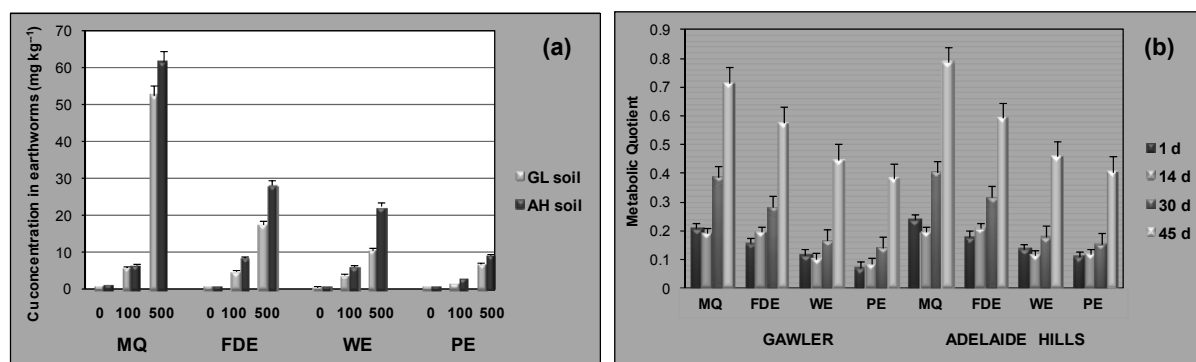


Fig. 1a. Relationship between Cu in Gawler (GL) and Adelaide Hills (AH) soils and Cu in earthworms in the presence of MQ water and recycled water sources. b. Effect of recycled water sources and MQ water on metabolic quotient in Gawler and Adelaide Hills soils at 100 mg kg^{-1} Cu concentration.

CONCLUSIONS

The results clearly showed that recycled water sources decreased the inhibitory effect of Cu on earthworms and microorganisms, which is attributed to the formation of Cu-DOC complexes which are not readily bioavailable.

REFERENCES

- Anderson, J.P.E., Domsch, K. (1975). Measurement of bacterial and fungal contributions to respiration of selected agricultural and forest soils. *Can. J. Microbiol.* 21: 314-322.
- Anderson, J.P.E., Domsch, K. (1978). A physiological method for the quantitative measurement of microbial biomass in soils. *Soil Biol. Biochem.* 10: 215-221.
- Anderson, T.H., Domsch, K. (1990). Application of eco-physiological quotients (qCO₂ and qD) on microbial biomasses from soils of different cropping histories. *Soil Biol. Biochem.* 22: 251-255.
- Bloem, J., Hopkins, D.W., Benedetti, A. (2006). Microbiological methods for assessing soil quality. Wallingford, UK: CABI Publishing.
- Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, T., McDowell, R., Senesi, N. (2011) Dissolved organic matter: biogeochemistry, dynamics and environmental significance in soils. *Adv. Agron.* 110: 1-75.
- Hund-Rinke, K., Lindemann, M., Simon, M. (2005). Experiences with Novel Approaches in Earthworm Testing Alternatives. *J. Soils Sediments* 5: 233-239.
- Naidu, R., Bolan, N.S., Megharaj, M., Juhasz, A.L., Gupta, S., Clothier, B. and Schulin, R. (2008). Chemical bioavailability in terrestrial environments. In "Chemical Bioavailability in Terrestrial Environment" (R. Naidu *et al.*, Eds.). pp. 1-6. Elsevier, Amsterdam, The Netherlands.
- Vance, E., Brookes, P., Jenkinson, D. (1987). An extraction method for measuring soil microbial biomass C. *Soil Biol. Biochem.* 19: 703-707.

PESTICIDE RESIDUES IN COMPOST AND VERMICOMPOST FROM ORGANIC WASTE IN NORTHEAST THAILAND

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INTRODUCTION

The objective of this study aims to monitor pesticide residues in organic waste in Northeast Thailand. Pesticides are widely used in agriculture and trade of agricultural products to increase agricultural yield and to protect plants from diseases, weeds and insect damage. The increasing use of pesticides has significantly increased crop contamination and human health hazard. On the Thai markets, fruit and vegetables have high risk for pesticide contamination. Uneatable and unusable parts of these goods transform to a fraction of organic waste. The quantity of waste in terms of solid waste from Northeast Thailand was 11,820 tons/day and over 50% was organic waste. Composting (such as compost, biological fermentation fertilizer) and animal feed are conventional methods to manage waste from vegetables and fruit in Northeast Thailand. The degradation of pesticide residues (cypermethrin deltamethrin and chlorpyrifos) in two types of composting were studied. Pesticide residue was analyzed by gas chromatograph. The first day of composting process, cypermethrin in the compost and vermicompost were found 1.864 and 0.873 mg/kg, respectively. After 60 days, the average degradation of cypermethrin were 94 and 100%, respectively. The first day of composting process, chlorpyrifos in the compost and vermicompost were found 0.392, and 0.184 mg/kg, respectively. After 60 days, the average degradation of chlorpyrifos were 72, and 100 %, respectively. The first day of composting process, deltamethrin in the compost, and vermicompost were found 0.101 and 0.047 mg/kg, respectively. After 60 days, the average degradation of deltamethrin were 100% in all composts. Therefore, the monitoring program for pesticide residues in organic waste are needed for sustainable management and protection of human's health and the environment.

METHODS

Sample collection

The selection of the samples was based on the typical composition of organic waste. The samples chosen for analysis should match the fractions presenting a high percentage of the total organic waste. The samples were collected from three main markets in Khon Kaen province, Northeast Thailand in winter season in 2010. Altogether, the compost, and vermicompost made from organic waste (cabbages, lettuce, kale and peel corn) were analyzed in three replicates by using the QuEChERS method (Anastassiades, et al., 2003).

Chemicals

Hexane, ethyl acetate and acetonitrile (PR grade), sodium chloride (analytical grade), magnesium sulfate anhydrous, primary secondary amine (PSA) and DI water were used for the pesticide extraction process.

Extraction and clean up

To prepare the samples, 10g of a previously homogenized food material sample was transferred into a suitable vessel and filled with fifteen milliliters of acetonitrile 10 ml and DI water 10 ml. The vessels were capped before mixing on a Vortex mixer for 2 min at optimum speed. Once the initial sample mixing was completed, 10 g NaCl and 6 g anhydrous MgSO₄

were added and immediately mixed on a Vortex mixer for 2 min and Shake for 4 hours on Shaker. To separate the phases, the samples were centrifuged for 5 min at 4000 rpm. Using an adjustable repeating pipette, 5.0 ml aliquot of upper acetonitrile layer was transferred into a 15 ml centrifuge tube containing 900 mg anhydrous MgSO₄ and 300 mg PSA sorbent. The centrifuge tube was tightly capped and shaken on a Vortex mixer for 1 min before the extracts (or the batch of extracts) were centrifuged for 5 min at 4000 rpm to separate the solids from the solution. The solution was then transferred into a vial for Gas Chromatograph (GC) analysis.

RESULTS AND DISCUSSION

The analyses revealed that most of the samples contained pesticide. Residues were found in 100% of the samples from mixed organic waste in three markets. Pesticide residues (mg kg⁻¹) were found in the different kinds of organic waste collected in Khon Kaen province. Pesticide residue in organic waste was found to be higher in the winter season than in the rainy season. The most frequently found pesticides were cypermethrin followed by chlorpyrifos, deltamethrin and lambda-cyhalothrin, respectively ranging from 0.044 to 2.608 mg kg⁻¹. Most pesticides were recovered in the range of 70% – 110% with relative standard deviation (RSD) usually less than 10%.

CONCLUSIONS

Organic waste contains a variety of pesticides some of which are banned from the Thai market (year 2006). In the composting process, pesticides might be degraded or mineralized. However, they might also be persistent to biological degradation and still occur in the process. Although, pesticide residues analyses in organic wastes are not legally required, a hidden and uncontrolled input of pesticide to soil environment might take place. Generally, organic waste products are considered environmental friendly as they are one of waste management solution. However, persistent pesticides introduced into this agricultural system might appear in the product and affect human health. Therefore, a monitoring program for pesticide residues and risk assessment study in organic waste are needed for protection of human's health and environment.

ACKNOWLEDGEMENTS

This work was supported by the Higher Education Research Promotion and National Research University project of Thailand, Office of the Higher Education Commission. The authors wish to express their sincere thanks to Khon Kaen University and Research Center for Environmental and hazardous substance management, Khon Kaen University. We wish to specifically thank to Prof. Nanthi Bolan for his kind help.

REFERENCES

- Anastassiades, M., Lehotay, S.J., Stajnbaher, D. and F. J. Schenck. (2003). Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce, *J. AOAC Int.* (86) : 412 - 431.
- Office of Natural Resources and Environment Khon Kaen . (2009). Solid waste management. [Online serial], Retrieved July 5, 2010 from the world wide web: <http://www.khonkhaenmnre.go.th>
- Pollution Control Department, Ministry of Natural Resources and Environment.(2010). Solid waste management. [Online serial], Retrieved July 5, 2010 from the world wide web: <http://www.pcd.go.th>



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