CL:AIRE Annual Project Conference
April 20th 2004

Cruciform Building
University College, London

Programme

0930 – 1015	Registration and coffee
1015 – 1020	Welcome and Introduction (Dr Graham Norris – Chief Executive, CL:AIRE)

Morning Session (Chair – Dr Gordon Lethbridge, Shell Global Solutions)

1020 – 1040	Intra-plume test facility (IPTF) to assess natural attenuation and remediation – Dr Mike Rivett/Chris Collinson, University of Birmingham
1045 – 1105	*Ex situ* soil vapour extraction to remediate chlorinated hydrocarbons – Richard Croft, Remedx Ltd and Paul Noble, ABB
1110 – 1130	Sustainable urban brownfield regeneration: integrated management (SUBR:IM) – Mike Brown/Dr Colin Smith, University of Sheffield
1135 – 1155	Cost effective investigation of contaminated land – Professor Mike Ramsey/Dr Paul Taylor, University of Sussex
1200 – 1315	**Lunch**

Afternoon Session (Chair – Steve Smith, Welsh Development Agency)

1315 – 1335	Passive treatment of acidic, aluminium-rich mine site drainage – Professor Paul Younger, University of Newcastle
1340 – 1410	*In situ* source treatment for enhanced bioremediation processes (INSTEP) – Professor Bob Kalin, Queen's University Belfast Indigenous microbial response to *in situ* remedial technologies (IMPART) – Dr Ian Thompson, NERC-CEH Oxford
1415 – 1435	Development of an *in situ* aquifer assessment tool – Professor Steve Banwart, University of Sheffield and Dr Paul Nathanail, University of Nottingham
1440 – 1515	**Break**
1515 – 1535	*In situ* bioremediation using engineered sequenced reactive barrier techniques – Professor Bob Kalin, Queen's University Belfast
1540 – 1600	Ferric iron remediation and stabilisation system (FIRS) – an electrokinetic technique – Dr Andrew Cundy, University of Sussex and Dr Laurence Hopkinson, University of Brighton
1605 – 1625	Performance assessment of stabilised/solidified waste-forms (PASSiFy) – Dr Colin Hills, University of Greenwich
1630	Close

This Conference has been sponsored by the following organisations:
Atkins English Partnerships Environment Agency Environmental Simulations International Ltd
Land and Water Remediation Ltd RAW Consulting Ltd Shell Global Solutions Total UK Ltd

Biographical Note

Mr Chris Collinson

Mr Chris Collinson is a member of the Hydrogeology Research Group of the School of Geography, Earth and Environmental Science at the University of Birmingham. He completed his first degree, an MSci in Environmental Geology, at Imperial College, London. He is currently developing an experimental test facility for studying natural attenuation processes and transport- / remediation-related parameters. This research aims to provide a resource of UK-based field data to facilitate characterization of a range of organic contaminants in superficial aquifers in the UK. This work, which comprises his PhD study, reflects his primary interest in organic contaminant hydrogeology. He maintains a keen interest in many aspects of the earth and environmental sciences.

Dr Michael Rivett

Dr Michael Rivett is currently a Lecturer in Hydrogeology at the University of Birmingham, School of Geography, Earth and Environmental Sciences. After completing a BA in Chemistry (Oxford), he completed his PhD at the University of Birmingham concerning organic contamination of the Birmingham aquifer. He completed a 4-year post-doctoral study at the University of Waterloo, Canada on the “Solvents-in-Groundwater” research programme undertaking field contaminant transport experiments in the Borden aquifer. On returning to the UK he worked as a hydrogeologist for the Ridings Area of the Environment Agency for 3 years specialising in regulation of groundwater and land contamination. He joined the University of Birmingham in 1997. His research interests are mainly within organic contaminant transport and remediation in groundwater, including chlorinated solvents and other VOCs, natural attenuation, groundwater – surface-water interactions and NAPLs.

An Intra-Plume Test Facility (IPTF) To Assess Natural Attenuation and Remediation

Michael Rivett, Chris Collinson, John Tellam,
Gareth Digges La Touche

School of Geography, Earth &
Environmental Sciences

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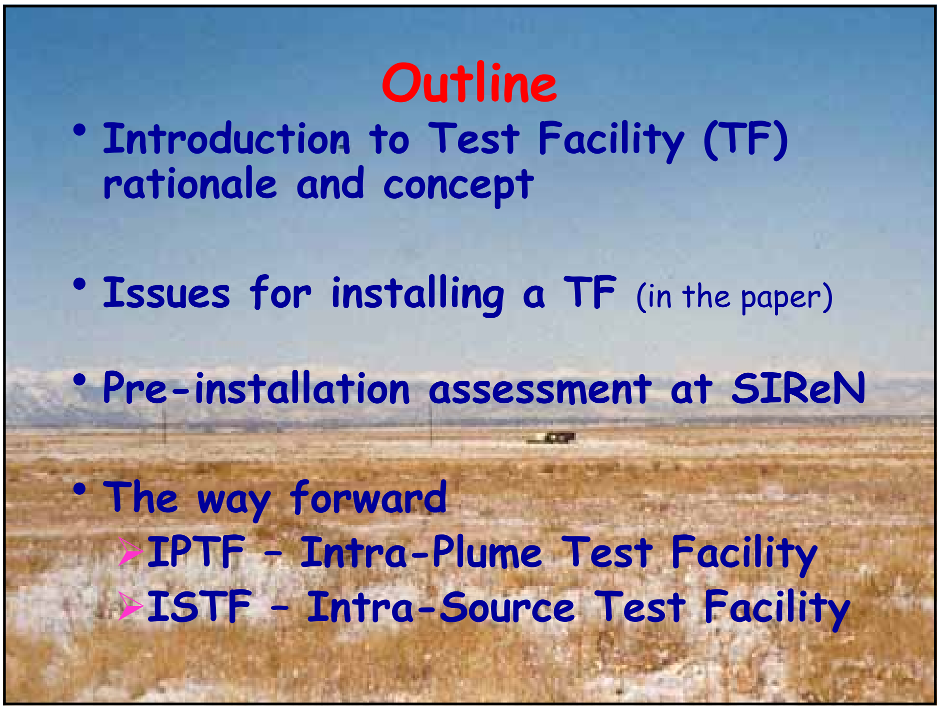


Outline

- Introduction to Test Facility (TF) rationale and concept
- Issues for installing a TF (in the paper)
- Pre-installation assessment at SIReN
- The way forward
    - IPTF – Intra-Plume Test Facility
    - ISTF – Intra-Source Test Facility

Prohibition of injection of List I due to Groundwater (EC GW Directive)

"The Scientific Polluters"

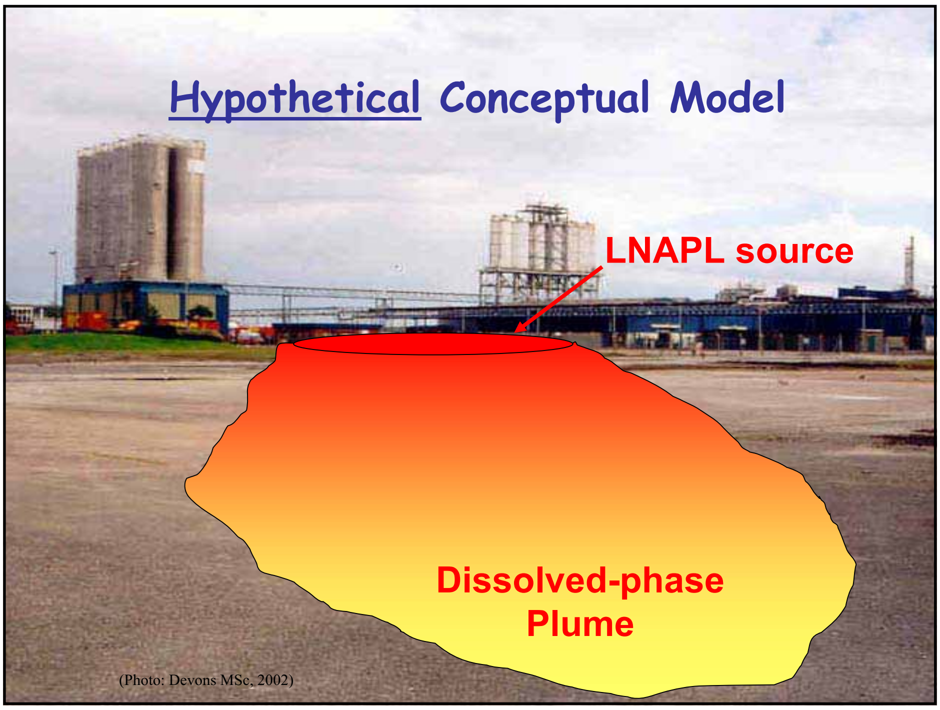
- **Canada** (Mackay et al.,1986; Rivett et al., 2001; and many others)
- **USA,** (MacIntyre et al., 1993)
- **Australia** (Thierrin et al., 1995)
- **and even Denmark** (Rügge et al., 1999; and others).

- **But not Here,** if you want list I in field
  - → use existing plumes kindly provided by industry…

SIReN

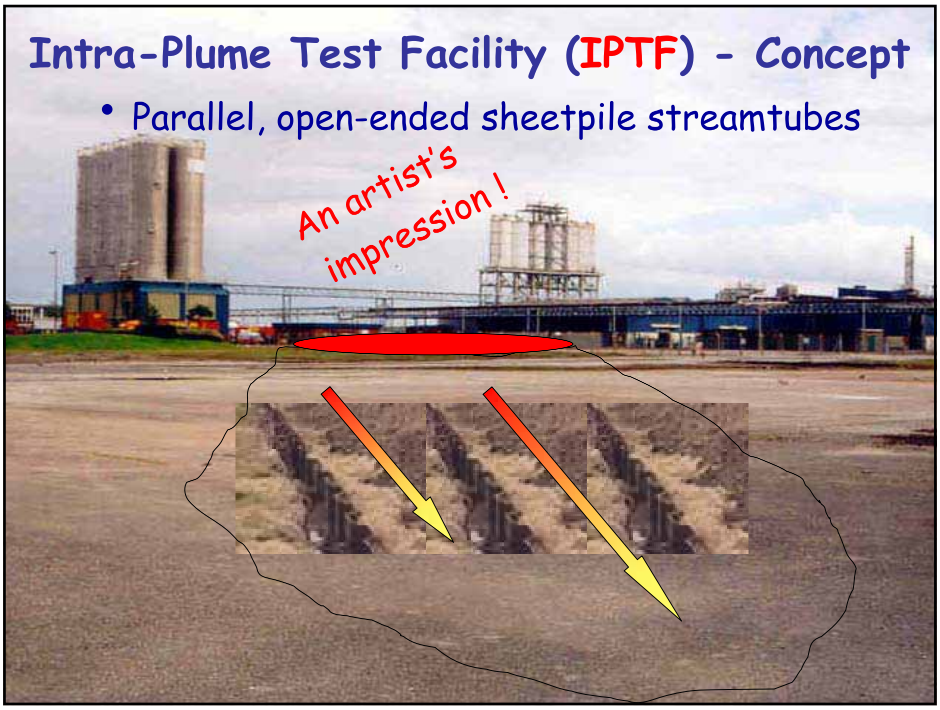
Site for Innovative Research into Natural Attenuation

(Photo: Devons MSc, 2002)



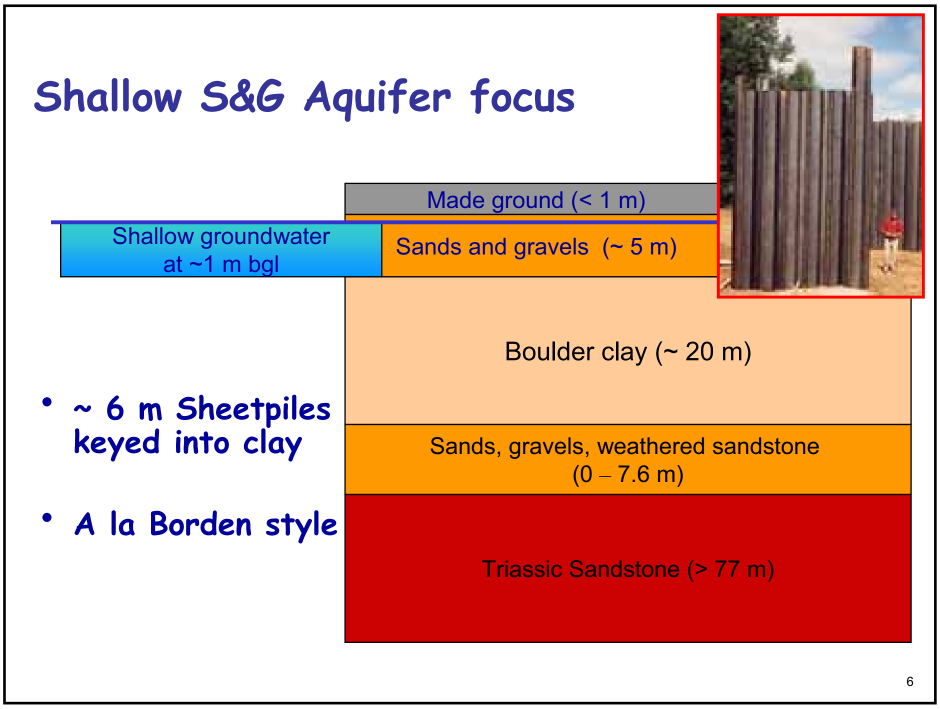
Hypothetical Conceptual Model

(Photo: Devons MSc, 2002)



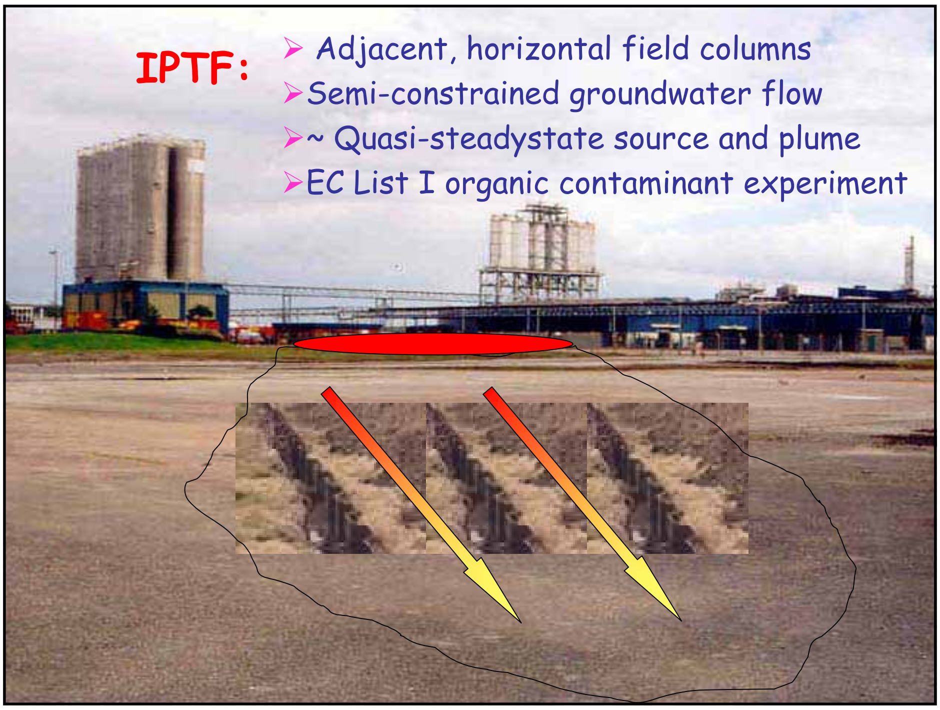
Intra-Plume Test Facility (IPTF) - Concept

- Parallel, open-ended sheetpile streamtubes



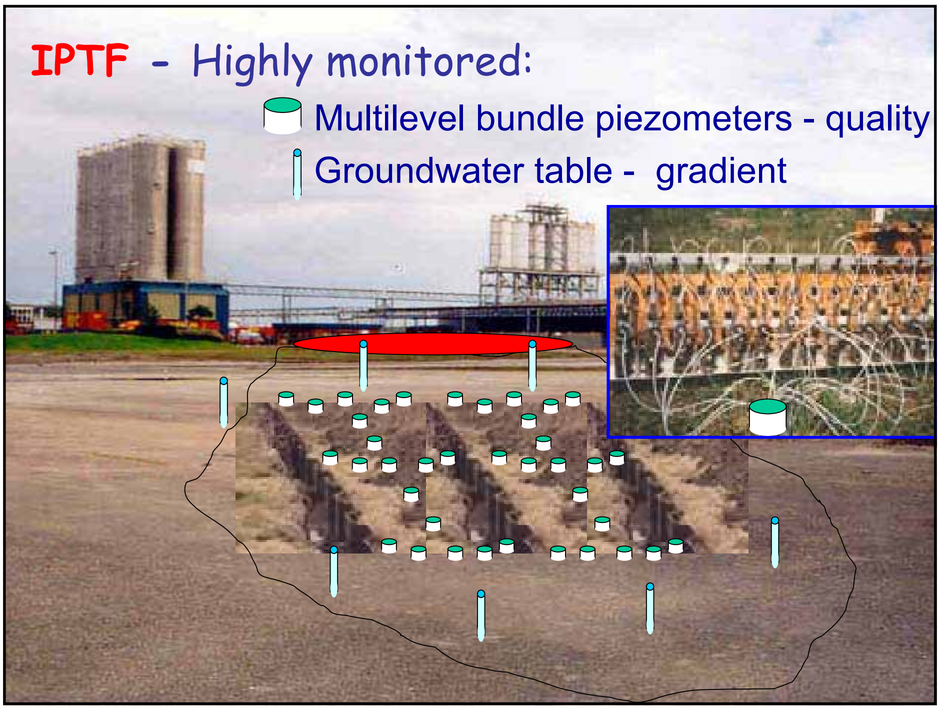
Shallow S&G Aquifer focus

- **~ 6 m Sheetpiles keyed into clay**
- **A la Borden style**



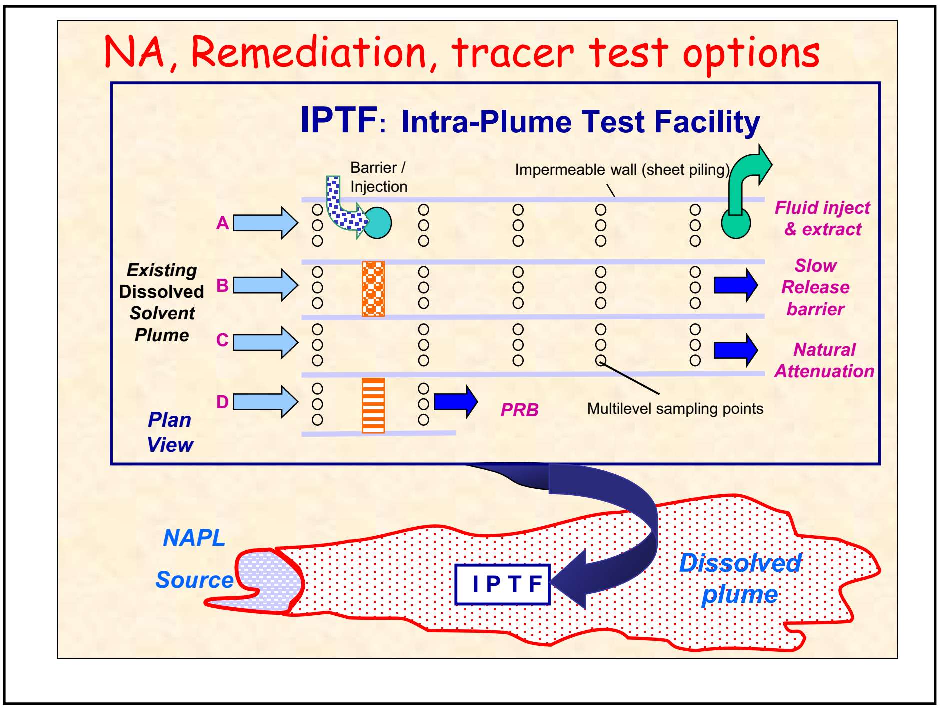
IPTF:

- Adjacent, horizontal field columns
- Semi-constrained groundwater flow
- ~ Quasi-steadystate source and plume
- EC List I organic contaminant experiment



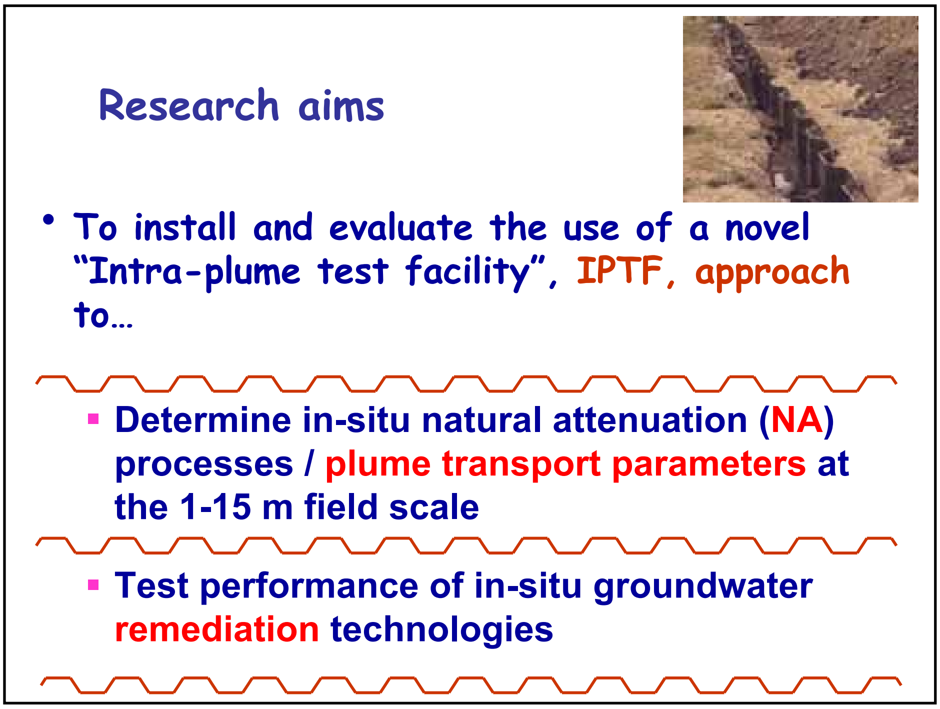
IPTF - Highly monitored:

- Multilevel bundle piezometers - quality
- Groundwater table - gradient



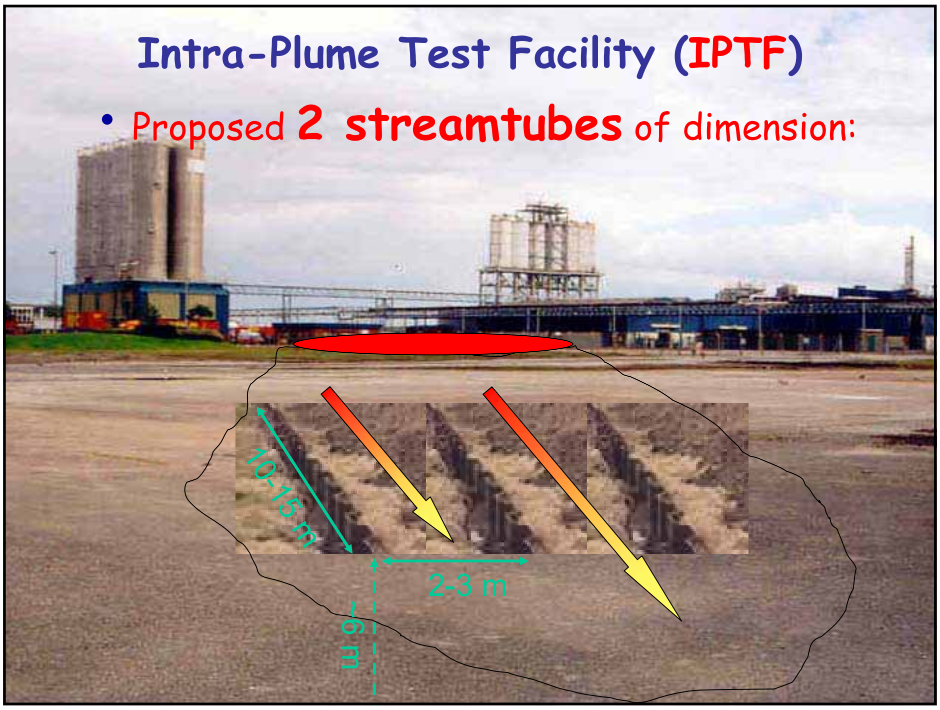
NA, Remediation, tracer test options

IPTF: Intra-Plume Test Facility



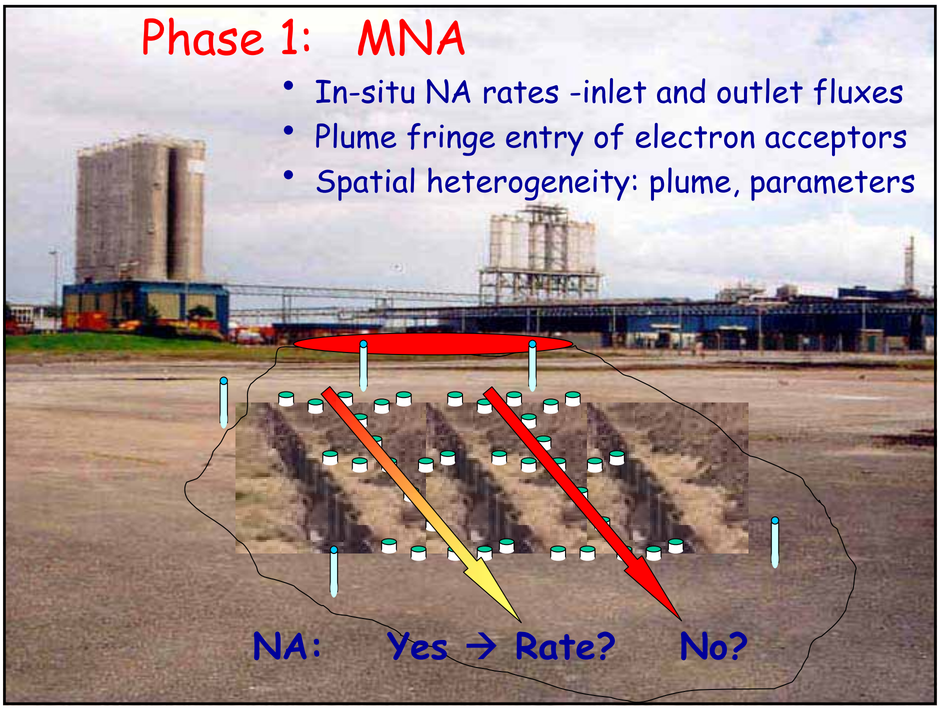
Research aims

- To install and evaluate the use of a novel "Intra-plume test facility", IPTF, approach to…
  - Determine in-situ natural attenuation (NA) processes / plume transport parameters at the 1-15 m field scale
  - Test performance of in-situ groundwater remediation technologies



Intra-Plume Test Facility (IPTF)

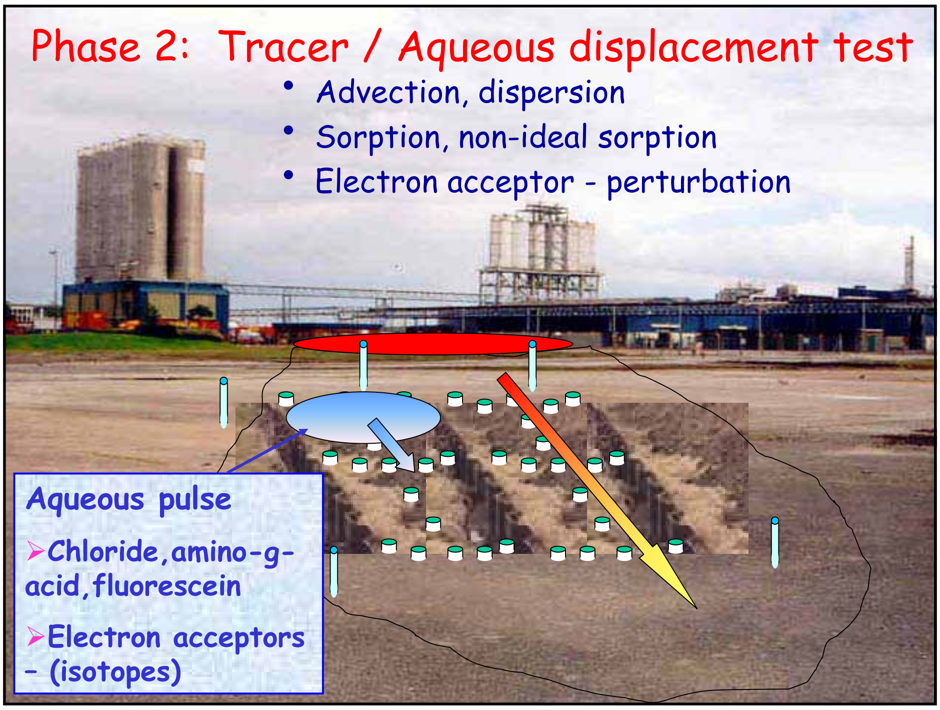
- Proposed **2 streamtubes** of dimension:



Phase 1: MNA

- In-situ NA rates -inlet and outlet fluxes
- Plume fringe entry of electron acceptors
- Spatial heterogeneity: plume, parameters

NA: Yes → Rate? No?



Phase 2: Tracer / Aqueous displacement test

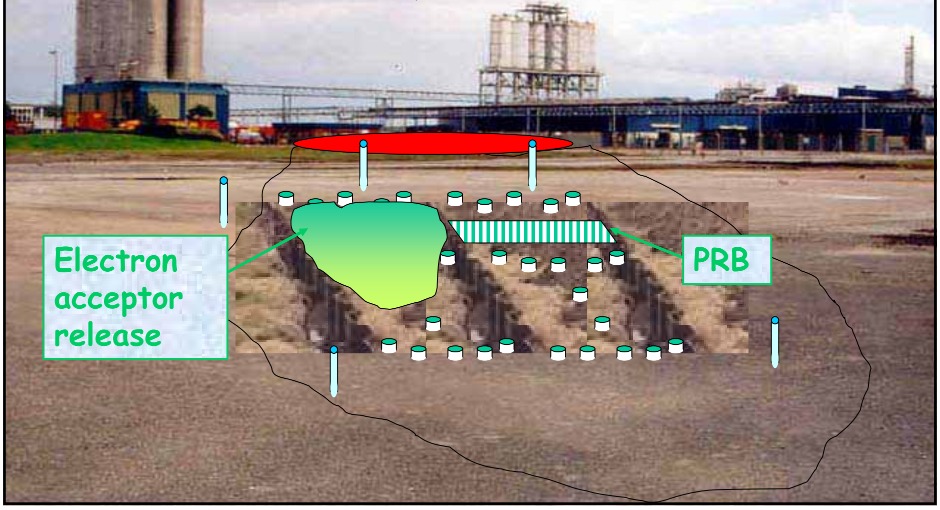
- Advection, dispersion
- Sorption, non-ideal sorption
- Electron acceptor - perturbation

Aqueous pulse

- **Chloride, amino-g-acid, fluorescein**
- **Electron acceptors - (isotopes)**

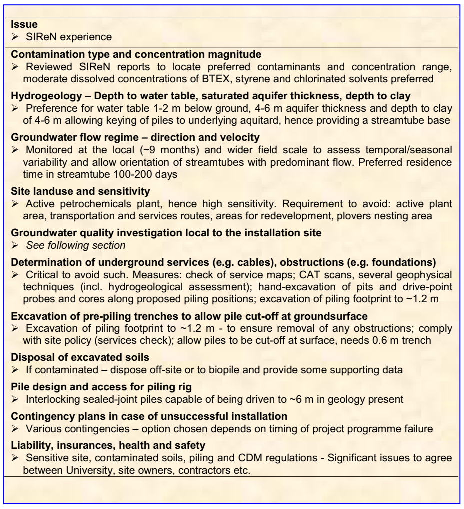
Phase 3: Remediation technology testing

- Likely an enhanced NA option
- PRB, electron acceptor release etc.
- Side-by side testing in known environment



Getting a TF (Test Facility) in the ground…

… Read the Paper…



Issue
- ➢ SIReN experience

Contamination type and concentration magnitude
- ➢ Reviewed SIReN reports to locate preferred contaminants and concentration range, moderate dissolved concentrations of BTEX, styrene and chlorinated solvents preferred

Hydrogeology – Depth to water table, saturated aquifer thickness, depth to clay
- ➢ Preference for water table 1-2 m below ground, 4-6 m aquifer thickness and depth to clay of 4-6 m allowing keying of piles to underlying aquitard, hence providing a streamtube base

Groundwater flow regime – direction and velocity
- ➢ Monitored at the local (~9 months) and wider field scale to assess temporal/seasonal variability and allow orientation of streamtubes with predominant flow. Preferred residence time in streamtube 100-200 days

Site landuse and sensitivity
- ➢ Active petrochemicals plant, hence high sensitivity. Requirement to avoid: active plant area, transportation and services routes, areas for redevelopment, plovers nesting area

Groundwater quality investigation local to the installation site
- ➢ *See following section*

Determination of underground services (e.g. cables), obstructions (e.g. foundations)
- ➢ Critical to avoid such. Measures: check of service maps; CAT scans, several geophysical techniques (incl. hydrogeological assessment); hand-excavation of pits and drive-point probes and cores along proposed piling positions; excavation of piling footprint to ~1.2 m

Excavation of pre-piling trenches to allow pile cut-off at groundsurface
- ➢ Excavation of piling footprint to ~1.2 m - to ensure removal of any obstructions; comply with site policy (services check); allow piles to be cut-off at surface, needs 0.6 m trench

Disposal of excavated soils
- ➢ If contaminated – dispose off-site or to biopile and provide some supporting data

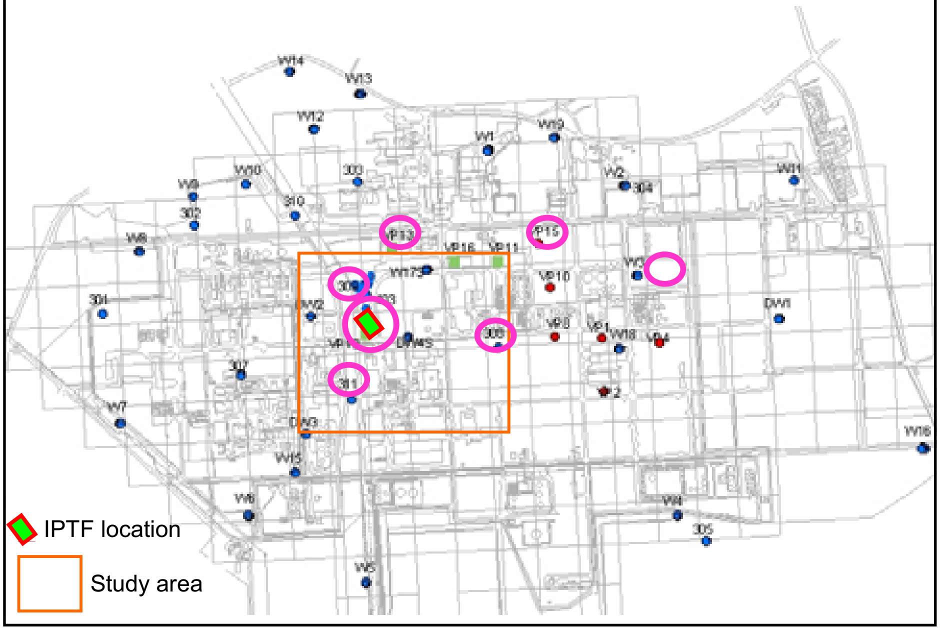
Pile design and access for piling rig
- ➢ Interlocking sealed-joint piles capable of being driven to ~6 m in geology present

Contingency plans in case of unsuccessful installation
- ➢ Various contingencies – option chosen depends on timing of project programme failure

Liability, insurances, health and safety
- ➢ Sensitive site, contaminated soils, piling and CDM regulations - Significant issues to agree between University, site owners, contractors etc.

- Contaminant type
- Hydrogeology
- GW flow regime
- Site landuse & sensitivity
- Advance investigations
- Underground services
- Excavate pre-piling trenches
- Disposal of excavated soils
- Piling issues
- Contingency plans
- Liabilities, H&S …

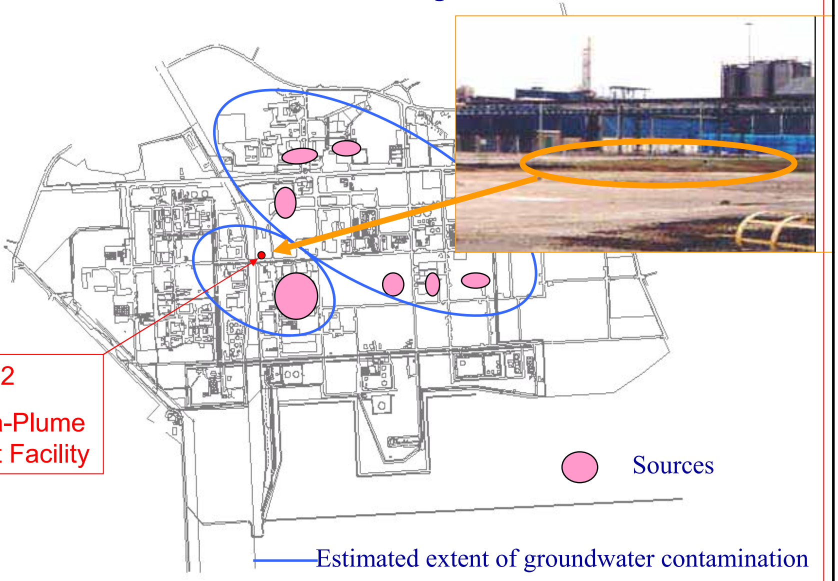
Candidate sites for TF ○



◆ IPTF location

☐ Study area

SIReN: Estimated extent of shallow groundwater contamination



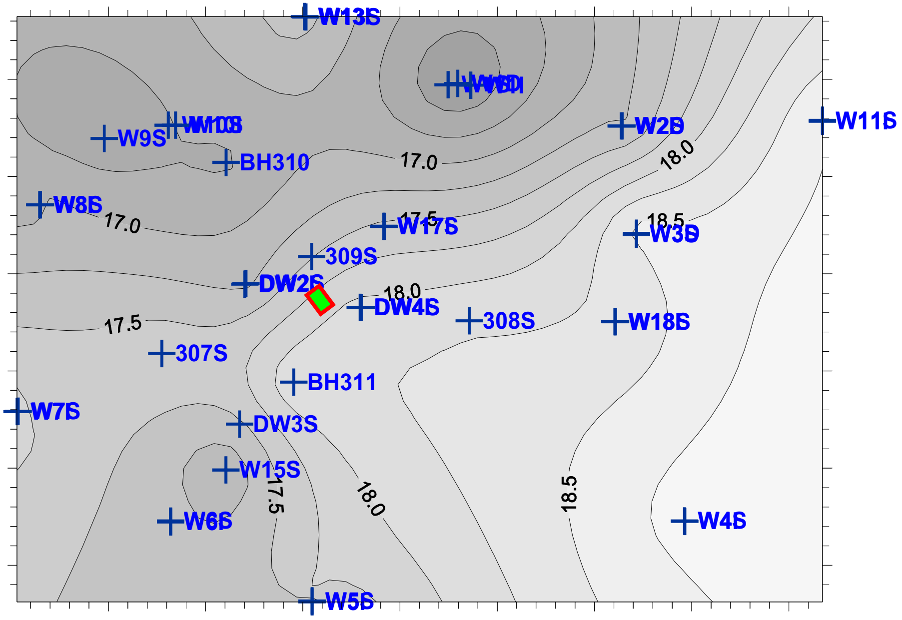
VP12

Intra-Plume Test Facility

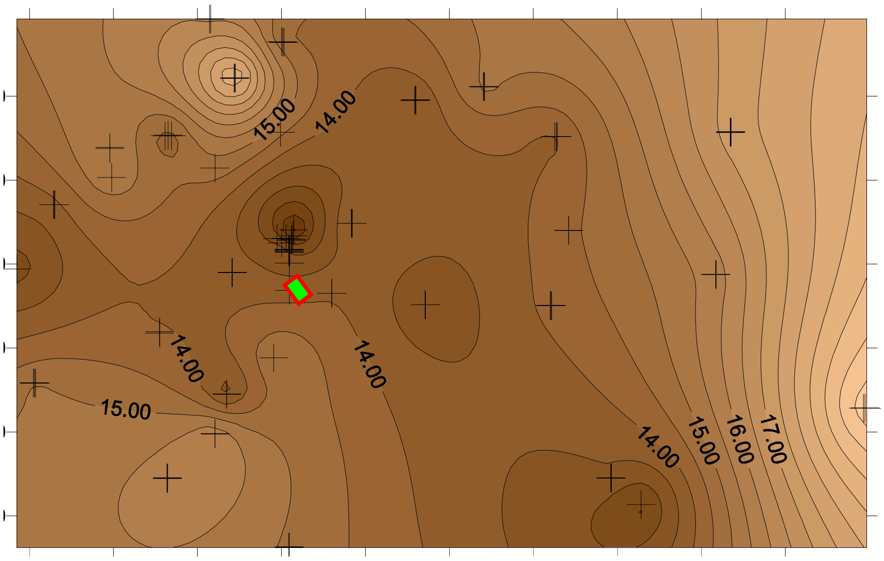
● Sources

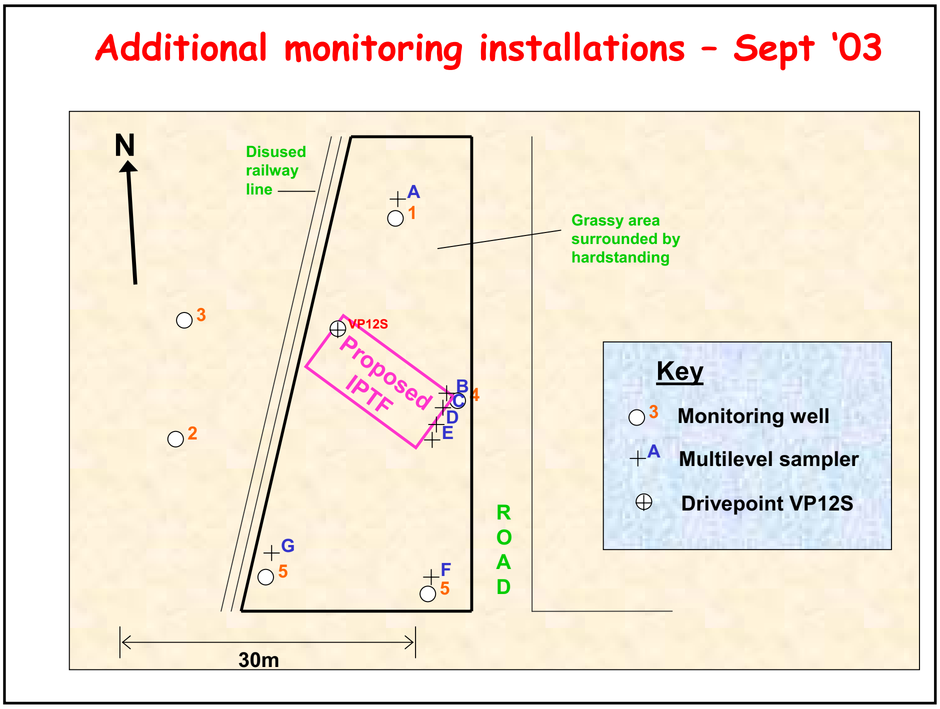
— Estimated extent of groundwater contamination

April 2003: Shallow Groundwater Elevations

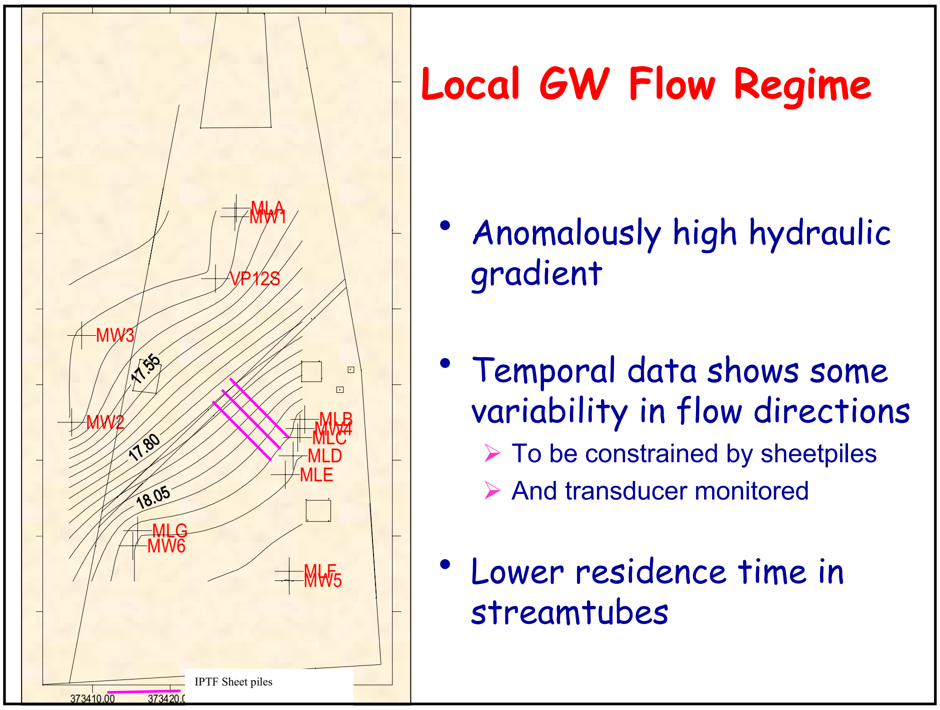


Clay Surface Elevation (m) – Below sand aquifer





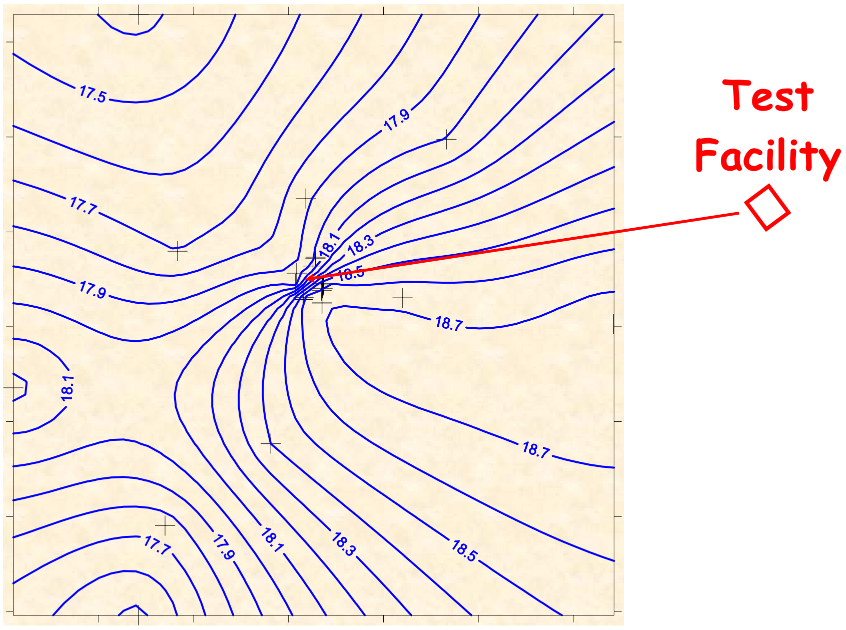
Additional monitoring installations – Sept '03



Local GW Flow Regime

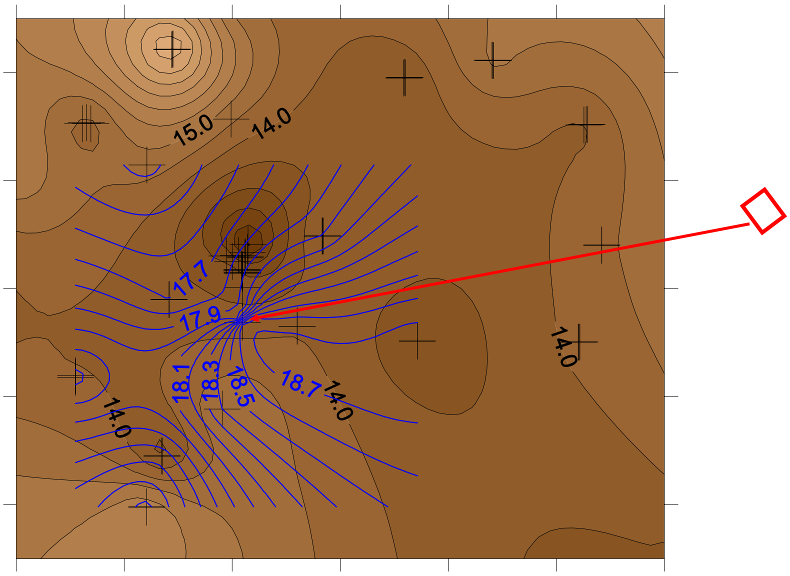
- Anomalously high hydraulic gradient
- Temporal data shows some variability in flow directions
  - To be constrained by sheetpiles
  - And transducer monitored
- Lower residence time in streamtubes

Water Table local to TF

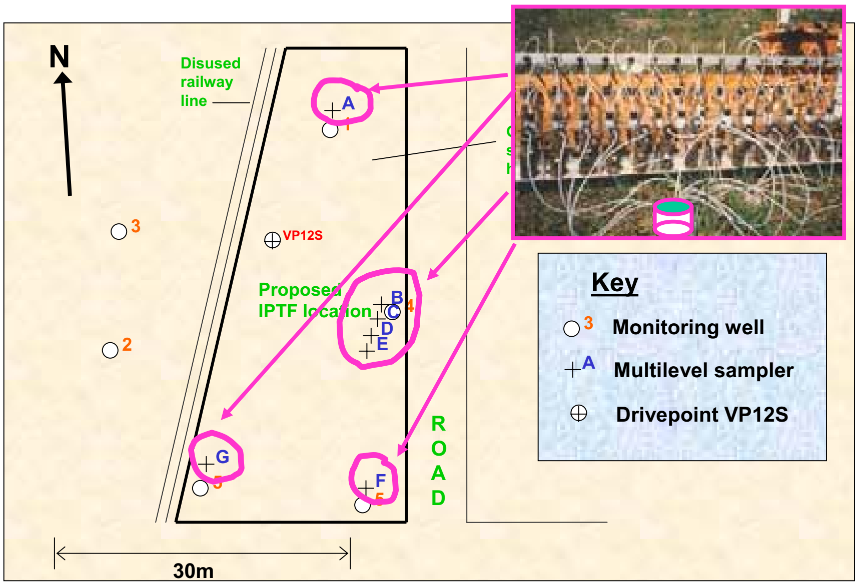


Test Facility

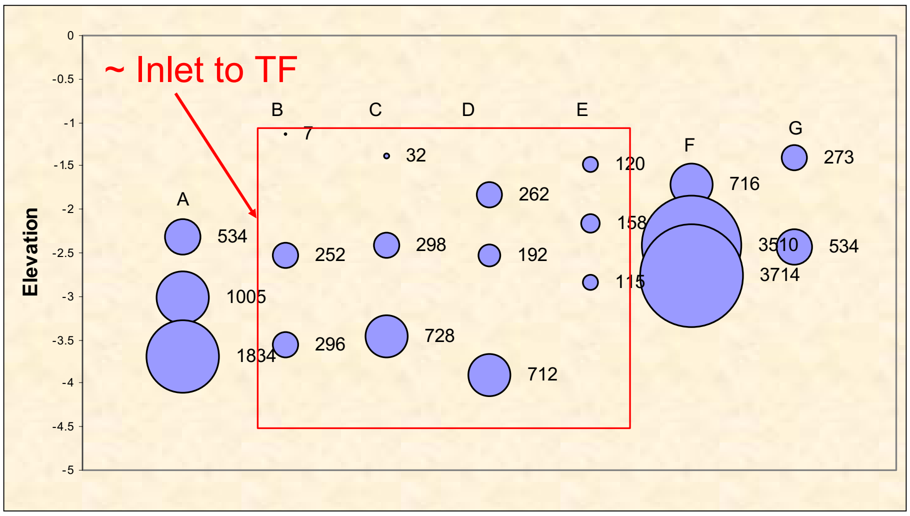
Water table - Clay Surface Relationships



Preliminary Multilevel sampling

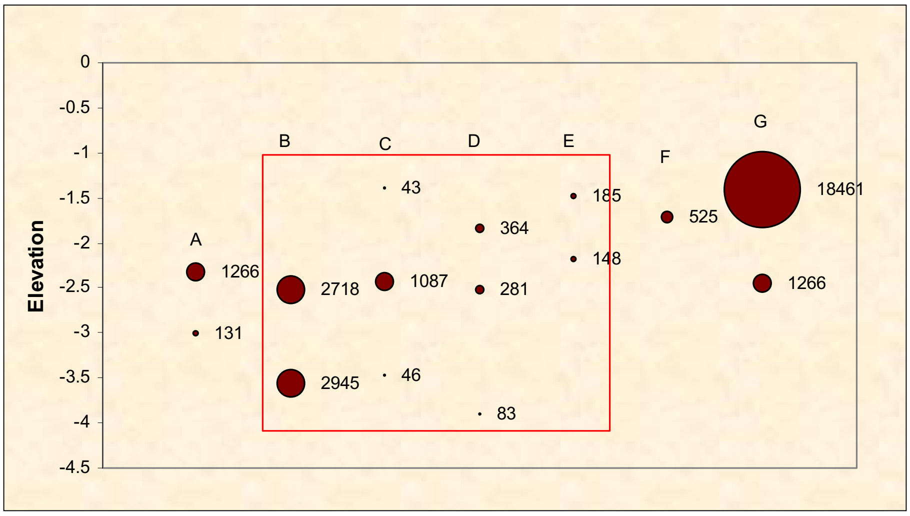


Benzene (μg/l)



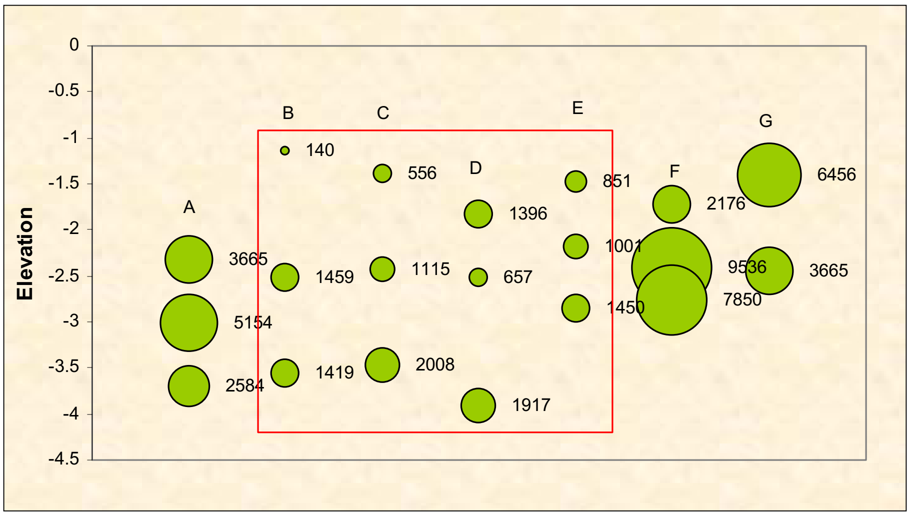
- Generally low concentrations at TF location,
- Slightly increasing with depth

Toluene (µg/l)



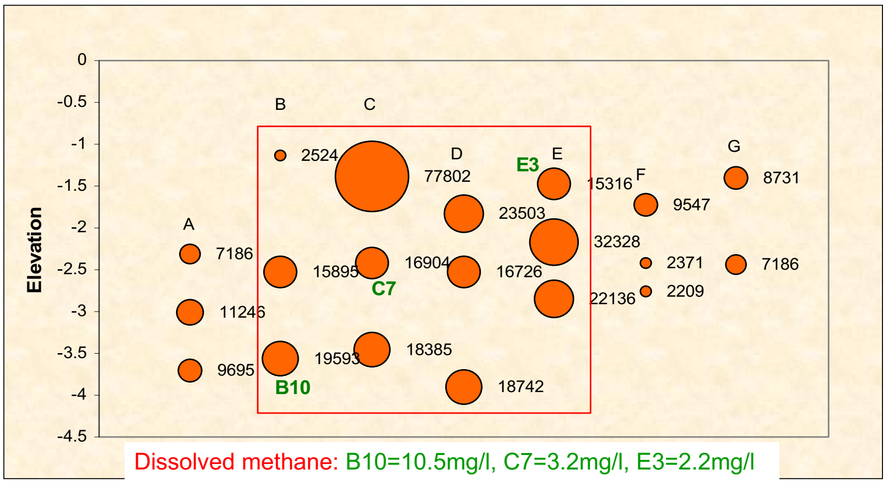
- Generally low concentrations at TF location,
- Exterior hotspot at multilevel G, 18.5 mg/L

Ethylbenzene (µg/l)



- Low concentrations consistently at TF location,
- No depth relationship obvious

Naphthalene (µg/l)

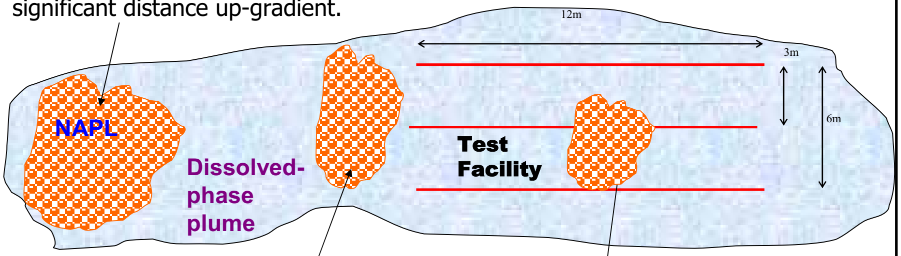


Dissolved methane: B10=10.5mg/l, C7=3.2mg/l, E3=2.2mg/l

- Naphthalene very high Solubility: 32 mg/L (solid); X_{naph} x 174 mg/L (NAPL)
- Indicative of source material, eg NAPL, closeby

Test Facility Configuration…

Relative to Source zones



Scenario 1. NAPL source present a significant distance up-gradient.

Scenario 2. NAPL source present up-gradient, but in close proximity to, the TF.

Scenario 3. NAPL source within TF.

Implications of preliminary data

- Very high naphthalene and TPH indicates source in TF or in close proximity
- Move to a new location? …
- Develop an Intra-Source Test Facility (ISTF) now
- Apply for Intra-Plume Test Facility (IPTF) as a follow on research grant…
- If floating LNAPL source may find TF has:
  - Source-based ISTF character in upper horizons
  - Plume-based IPTF character at deeper horizons

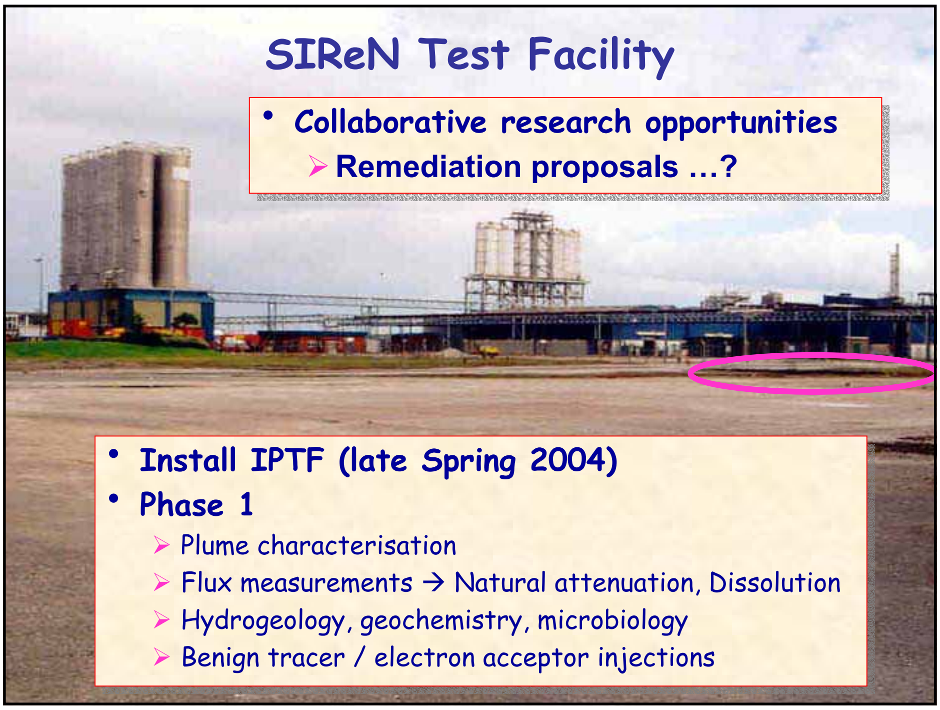
Intra-Plume Test Facility (IPTF)

- Delineation of dissolved-phase plume and electron acceptors spatial heterogeneity
- Determination of dispersion via benign tracer injections.
- Determination of sorption controls via aqueous injection plume displacement tests (akin to pump-and-treat)
- Determination of dissolved-plume fluxes and NA / (bio)degradation occurrence
- Evaluation of responses to pulse injections of plume-depleted electron acceptors
- Remediation via enhanced NA with sustained electron acceptor releases
- Remediation via PRBs

Intra-Source Test Facility (ISTF)

- Delineation of NAPL sources and spatial heterogeneity via partitioning tracer tests; geophysics, laser-induced fluorescence
- Determination of NAPL source dissolution fluxes and controlling processes
- For multi-component NAPLs, evaluation of Raoult's Law applicability and aqueous-NAPL re-equilibration
- High concentration influences on sorption
- High concentration / NAPL influences on biodegradation rates
- Remediation via enhanced NAPL solubilisation, e.g. surfactants, alcohols
- Remediation via in-situ NAPL destruction, e.g. in-situ chemical oxidation

More demanding really compared to IPTF…



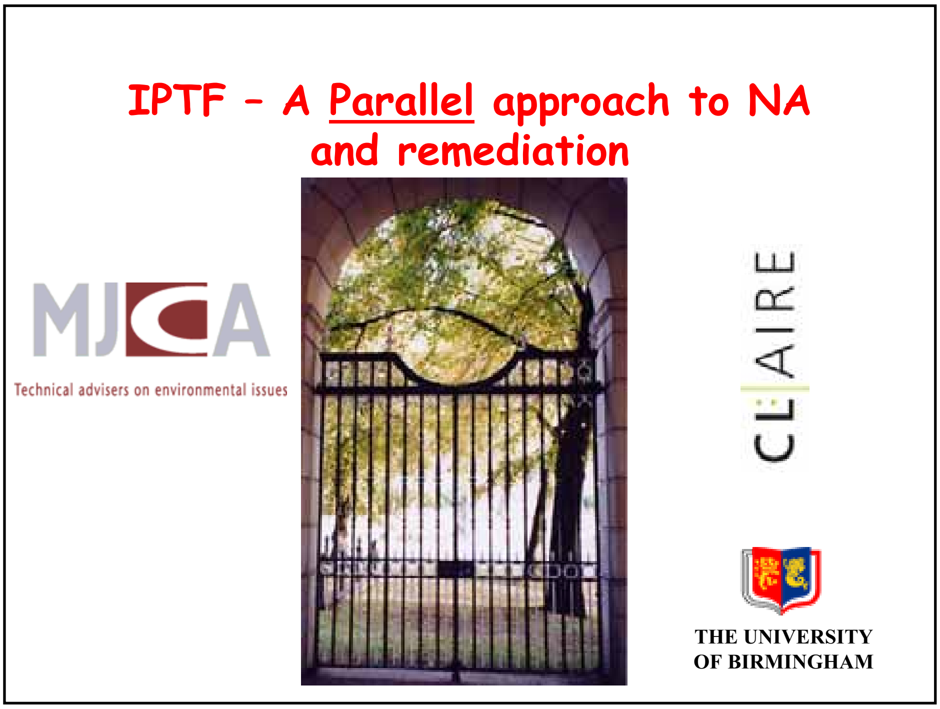
SIReN Test Facility

- **Collaborative research opportunities**
  - **Remediation proposals …?**

- **Install IPTF (late Spring 2004)**
- **Phase 1**
  - Plume characterisation
  - Flux measurements → Natural attenuation, Dissolution
  - Hydrogeology, geochemistry, microbiology
  - Benign tracer / electron acceptor injections

An Intra-Plume Test Facility (IPTF) To Assess Natural Attenuation and Remediation

Michael Rivett and Chris Collinson



IPTF – A Parallel approach to NA and remediation

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Developing an Intra-Plume Test Facility (IPTF) to Assess Contaminant Natural Attenuation and Remediation

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ABSTRACT

The intra-plume test facility (IPTF) and intra-source test facility (ISTF) concepts are introduced as novel field-scale methods to assess contaminant natural attenuation and remediation. The approaches are compared and issues presented that require consideration for a successful TF installation. Initial site data obtained local to the proposed TF installation site at the UK's SIReN, site ("Site for Innovative Research in Natural Attenuation") are presented. The TF is to be installed in 2004 to assess the aromatic hydrocarbons present.

INTRODUCTION

Field experiments involving injection of toxic organic chemicals of health concern into groundwater are not permitted in the UK as they contravene the EC Groundwater Directive that prohibits intentional discharge of List I substances to groundwater in Europe. Such studies have, however, been undertaken elsewhere, e.g. Canada (Mackay et al.,1986; Rivett et al., 2001; and many others), USA, (MacIntyre et al., 1993), Australia (Thierrin et al., 1995) and even Denmark (Rügge et al., 1999; and others). Enormous scientific benefit has been derived from these tests arising from the known source conditions and intensive monitoring. Whilst one may debate that controlled field-injection research experiments should be exempted from the Groundwater Directive prohibition, it still remains critical to develop alternative field methods to evaluate groundwater-contaminant transport processes and reliably estimate associated parameters that control migration and "natural attenuation" (NA) of plumes as well as the ultimate success of in-situ remediation attempts. Such a need provides the rationale for our research programme.

Our thesis is that controlled research within intentionally-isolated streamtubes of groundwater contamination that already exists at real sites provides a way forward to meet the above need. The original concept was to create an "intra-plume test facility" (IPTF) comprised of two or more adjacent streamtubes within a dissolved-phase organic solute downstream of a source area. We now also propose that the concept can be additionally extended to include NAPL (nonaqueous-phase liquid) source zones that generate dissolved plumes and that an "intra-source test facility" (ISTF) could also be built. Ultimately the proposal is to separately develop both test facilities (TFs), a plume-based IPTF and a source-based ISTF. At present, industrial funding has been secured to develop one of these TFs at the SIReN site. SIReN, the "Site for Innovative Research in Natural Attenuation", is a joint initiative between Shell, the Environment Agency, AEA Technology, supported by CL:AIRE to promote field-based research in monitored natural attenuation (MNA). The focus of initial phases of the TF research is to be on discernment of contaminant transport processes, particularly those of relevance to NA. Later, there will be a shift of emphasis at the characterised test facilities to the implementation and evaluation of remediation technologies. Presently the research is nearing installation of a TF at SIReN after an initial stage of site assessment.

The objectives of this paper are to: (i) outline the proposed groundwater streamtube test facility concept and compare source-base ISTF and plume-based IPTF approaches; (ii) discuss issues that require consideration for a successful TF installation; and (iii) review initial site assessment data obtained local to the proposed TF installation site at SIReN.

THE TEST FACILITY CONCEPT

The streamtube-based TF concept is shown in Fig. 1. It is a relatively simple concept, but not used to date in the format we propose. The closest equivalent is the sheetpile stream tube-based tracer injection – remediation experiment of Brown et al. (1999) undertaken at Borden, Canada. The TF is to be located within an existing contaminated plume and comprises a set of parallel rows of sheet piling aligned with the predominant site groundwater flow direction. Multiple streamtubes may be created adjacent to one another that may allow side-by-side comparisons. The adjacent "groundwater streamtubes" created are open both up-gradient and down-gradient; this allows near-natural flow of the existing contaminant plume through the streamtubes. Intensive monitoring, tracer-injection testing, and remediation technology testing within the constrained streamtube flow environment permit an array of controlled contaminant transport and remediation research options. A key advantage of the streamtube-based approach is the constrained groundwater flow environment that significantly reduces problems caused by vagaries in natural groundwater flow direction changes induced by seasonal or other spatially/temporally variable groundwater recharge or discharge events. Tracer tests conducted under natural gradient groundwater flow conditions have often suffered from such flow direction variability causing significant concentration variability at specific monitoring points (Rivett et al., 2001) and even plumes moving laterally beyond monitoring networks necessitating "plume chasing" (Leblanc et al. 1991; Rivett et al., 2001).

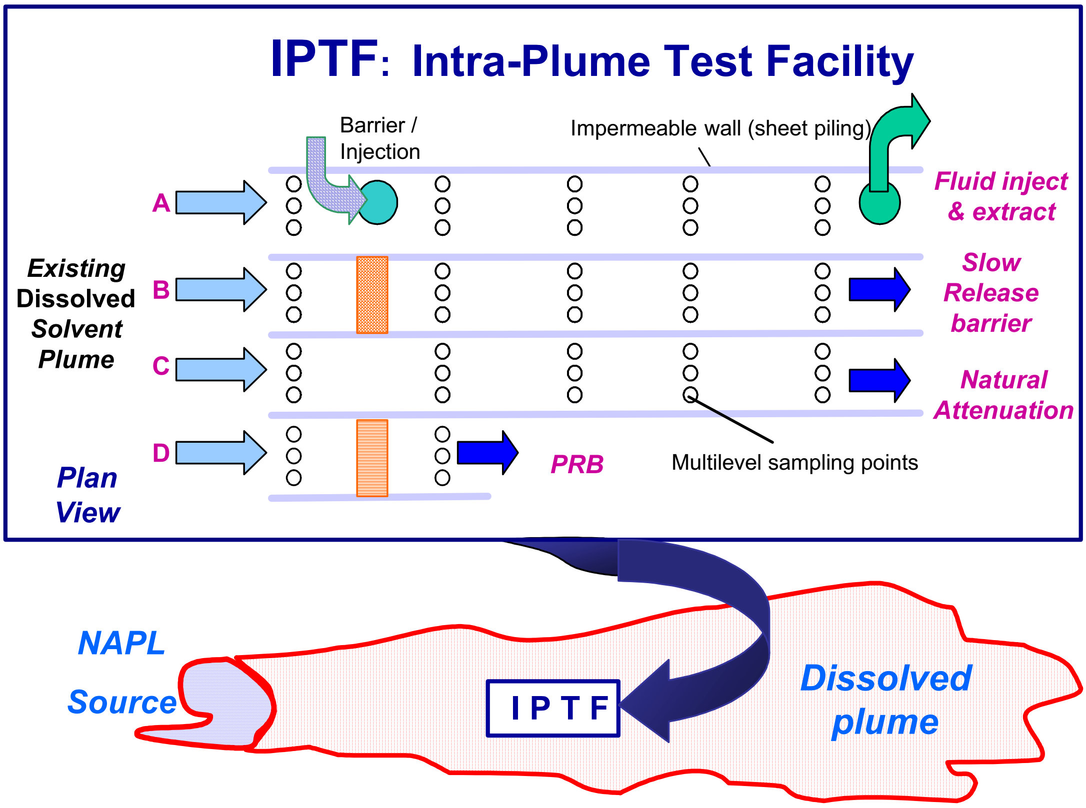


Fig.1. The groundwater streamtube test facility concept showing a variety of research possibilities for an intra-plume test facility (IPTF).

The piling-based TF is restricted to unconsolidated, shallow water table aquifers. Piles will be joint-sealed and preferably keyed into an underlying clay aquitard. Dimensions of streamtubes depend upon aquifer dimensions, groundwater velocities, contaminant types and funding availability; for the present research individual streamtubes are anticipated to be ~12 m pathlength, ~3 m wide and extend over an aquifer depth up to ~ 6 m. An array of multilevel samplers will be installed within each streamtube that allow point groundwater samples to be obtained from discrete depths allowing detailed longitudinal and transverse "fence" images of contaminant concentrations migrating through the streamtube to be collected. Concentration data combined with groundwater flow rate data will allow contaminant flux estimations at the various fences positioned along individual streamtubes and hence estimation of NA. Other tests or remediation technologies may also be implemented within streamtubes, for example: tracer tests with benign tracers; large-scale displacement of the resident plume by a large aqueous pulse (akin to pump-and-treat); enhanced NA remediation methods, permeable reactive barriers (PRBs) etc.

Comparison of intra-source and intra-plume test facilities

The ISTF and IPTF offer differing research possibilities. Research issues that could be potentially studied within these two facility types are compared in Table 1. Although the originally envisaged concept was for an IPTF, Table 1 illustrates that there are plenty of worthwhile research options for the ISTF approach although this latter facility type is both practically and technically more demanding.

Table 1. Examples of research issues for intra-source and intra-plume test facilities.

Intra-source test facility (ISTF)	Intra-plume test facility (IPTF)
▪ Delineation of NAPL sources and spatial heterogeneity via partitioning tracer tests; geophysics, laser-induced fluorescence	▪ Delineation of dissolved-phase plume and electron acceptors spatial heterogeneity
▪ Determination of NAPL source dissolution fluxes and controlling processes	▪ Determination of dispersion via benign tracer injections.
▪ For multi-component NAPLs, evaluation of Raoult's Law applicability and aqueous-NAPL re-equilibration	▪ Determination of sorption controls via aqueous injection plume displacement tests (akin to pump-and-treat)
▪ High concentration influences on sorption	▪ Determination of dissolved-plume fluxes and NA / (bio)degradation occurrence
▪ High concentration / NAPL influences on biodegradation rates	▪ Evaluation of responses to pulse injections of plume-depleted electron acceptors
▪ Remediation via enhanced NAPL solubilisation, e.g. surfactants, alcohols	▪ Remediation via enhanced NA with sustained electron acceptor releases
▪ Remediation via in-situ NAPL destruction, e.g. in-situ chemical oxidation	▪ Remediation via PRBs

Many contaminated sites are highly complex with a near ubiquitous potential for multiple source zones. A number of NAPL sources are often present that are often spatially heterogeneous, comprise smaller sub-sources and difficult to reliably locate, particularly if NAPL resides below the water table. Indeed it may be difficult to prove that a proposed TF location is completely free from NAPL sources without significant investigation, i.e. a proposed IPTF may ultimately prove to be an ISTF when detailed monitoring of multilevel samplers installed within the streamtube is undertaken. It is noted, however, that typically weak vertical dispersion of plumes (Rivett and Allen-king, 2003), may cause source zones restricted to discrete horizons of the streamtube, e.g. within 1-2 m of the water table, to act as an ISTF at such elevations and the deeper, source-free zone, to act as an IPTF at depth. This would clearly be beneficial and more probable in streamtubes isolating a greater depth of aquifer formation and in cases where just (light) LNAPL contamination is present near water table. These vertically distinct zones may be potentially discerned via conventional tracer and partitioning tracer tests. The issue of multi-sources and their discernment is judged important in relation to NA assessment and MNA strategies as missed sources may result in serious misinterpretations of site data and risks posed.

INSTALLATION OF A TEST FACILITY – ISSUES TO CONSIDER

Various issues need to be considered to facilitate a successful TF installation. The main issues considered are indicated in Table 2 and a brief comment relating to our SIReN experiences made. SIReN is a large (~1x2 km), active petrochemicals plant in the north-west of England (Jones et al., 1999). Much of the contamination at the site is within the shallow, water table unconsolidated aquifer comprised of mainly fine-medium sand with occasional gravel and silts. This is underlain by a variable thickness clay aquitard. It has to date proved challenging to find the ideal test facility site within SIReN and that a compromise is probable after reviewing in detail ~5 potential sites. The preferred site at present, referred to as VP12 (Lethbridge et al., 2003), is one that fulfils logistical criteria, but does display elevated concentrations that are symptomatic of very nearby sources, but not initially recognised as a source in early reports (Jones et al., 2001). Historical site plans later proved to indicate the area had been used for product storage.

Table 2. Considerations for a test facility installation and SIReN-relevant comment.

Issue	➢ SIReN experience
Contamination type and concentration magnitude	➢ Reviewed SIReN reports to locate preferred contaminants and concentration range, moderate dissolved concentrations of BTEX, styrene and chlorinated solvents preferred
Hydrogeology – Depth to water table, saturated aquifer thickness, depth to clay	➢ Preference for water table 1-2 m below ground, 4-6 m aquifer thickness and depth to clay of 4-6 m allowing keying of piles to underlying aquitard, hence providing a streamtube base
Groundwater flow regime – direction and velocity	➢ Monitored at the local (~9 months) and wider field scale to assess temporal/seasonal variability and allow orientation of streamtubes with predominant flow. Preferred residence time in streamtube 100-200 days
Site landuse and sensitivity	➢ Active petrochemicals plant, hence high sensitivity. Requirement to avoid: active plant area, transportation and services routes, areas for redevelopment, plovers nesting area
Groundwater quality investigation local to the installation site	➢ *See following section*
Determination of underground services (e.g. cables), obstructions (e.g. foundations)	➢ Critical to avoid such. Measures: check of service maps; CAT scans, several geophysical techniques (incl. hydrogeological assessment); hand-excavation of pits and drive-point probes and cores along proposed piling positions; excavation of piling footprint to ~1.2 m
Excavation of pre-piling trenches to allow pile cut-off at groundsurface	➢ Excavation of piling footprint to ~1.2 m - to ensure removal of any obstructions; comply with site policy (services check); allow piles to be cut-off at surface, needs 0.6 m trench
Disposal of excavated soils	➢ If contaminated – dispose off-site or to biopile and provide some supporting data
Pile design and access for piling rig	➢ Interlocking sealed-joint piles capable of being driven to ~6 m in geology present
Contingency plans in case of unsuccessful installation	➢ Various contingencies – option chosen depends on timing of project programme failure
Liability, insurances, health and safety	➢ Sensitive site, contaminated soils, piling and CDM regulations - Significant issues to agree between University, site owners, contractors etc.

ADVANCE SITE INVESTIGATION LOCAL TO THE PROPOSED TEST FACILITY

Contamination at SIReN is predominantly due to hydrocarbons, particularly the aromatics, but with occasional occurrences of low-concentration chlorinated solvents. In relation to the superficial sand aquifer, several LNAPL source zones have been identified (Jones *et al*., 2001) Some dissolved concentrations are high and symptomatic of nearby NAPL other site areas showed very limited or absent contamination (Jones *et al*., 2001; Lethbridge *et al*, 2003). The area around Geoprobe® point VP12S has been examined in detail and actively instrumented by ourselves as shown in Fig. 2 that indicates the proposed TF location at SIReN. Four multilevel samplers ~ 2m apart (10 sample points on each) were installed close to the proposed inlet of the TF and three other multilevels nearby. A number of additional water table observation wells were installed to determine the flow regime (Fig. 2). The flow regime delineated is orientated with the regional direction of flow, but apparently has increased gradients around the test facility location that have not been fully explained.

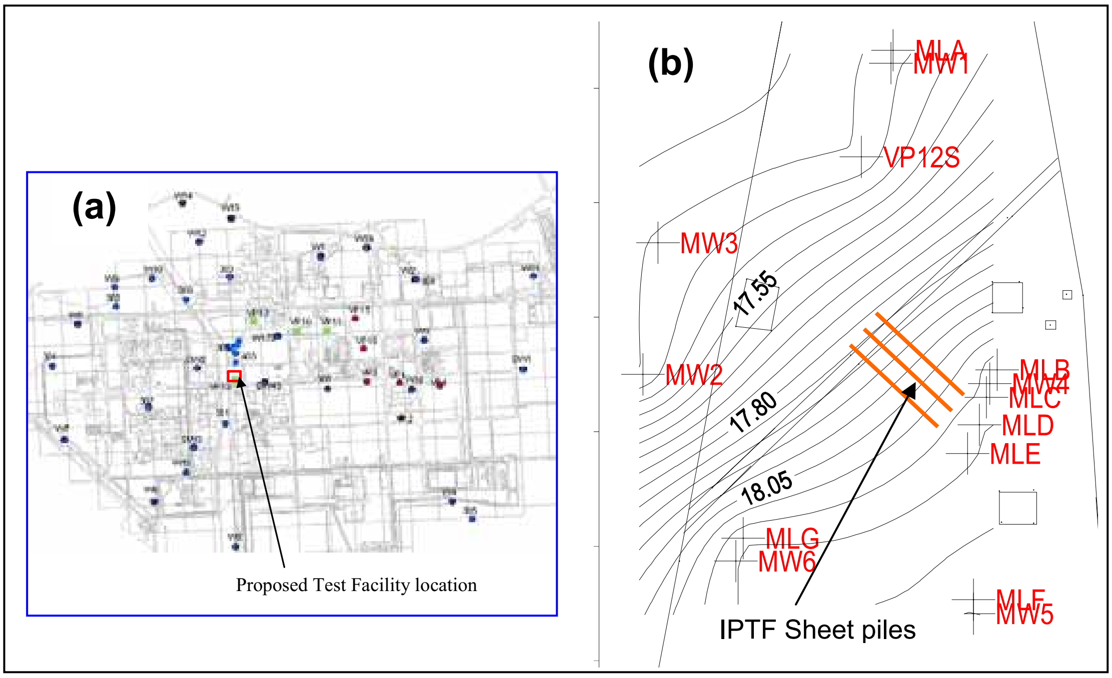


Figure 2. (a) Proposed Test Facility location at SIReN ; (b) Close up of Test Facility location showing monitoring and November 2003 water table (tic marcs at 10 m).

Concentration data from a selection of 20 points on the multilevels are shown in Fig. 3a and 3b. Concentrations vary by nearly 3 orders of magnitude for benzene and ethylbenzene. Concentrations for BTEX and styrene were consistently lower in the TF inlet multilevels than the other surrounding multilevels and represent acceptable dissolved-phase concentrations for an IPTF. Naphthalene data (Fig. 3b), however, show the reverse with extremely high concentrations detected in the TF inlet in particular. Naphthalene ranges from 2-78 mg/l which compares to its pure-phase aqueous solubility of 32 mg/l and a supercooled solubility (appropriate if dissolving from a multi-component NAPL source) of 174 mg/l. Such naphthalene values are indicative of nearby sources zones; i.e. the facility may prove to be an ISTF. Methane levels at 2-10 mg/l in the inlet TF multilevels indicate conditions have developed to a methanogenic status for which biodegradation for many aromatics is potentially absent or at best low. Further samples have recently been collected (data not available yet) to better verify concentration distributions, potential for sources, confirm extent of higher molecular weight hydrocarbons potentially present and evaluate other electron acceptor distributions.

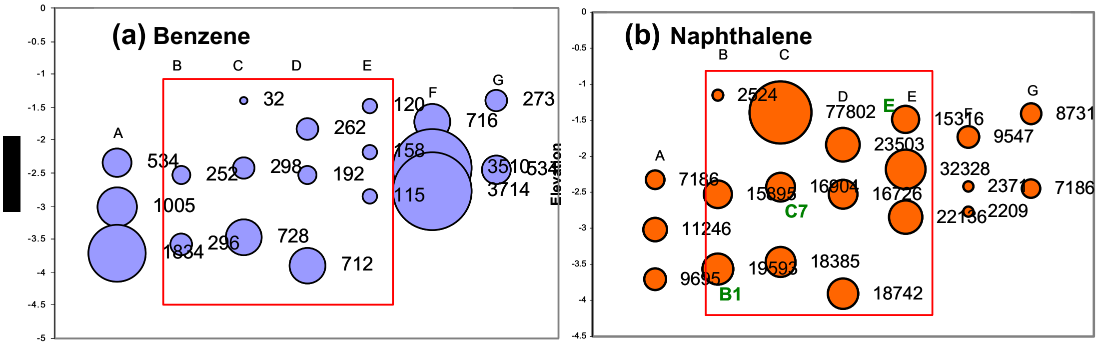


Figure 3. Concentrations (μg/l) in selected sampling points with multilevels B,C,D and E located at the entry of the proposed IPTF location: (a) Benzene; (b) Naphthalene.

CONCLUSIONS

The groundwater streamtube TF concept proposed is believed to be a useful and novel concept to evaluate transport and remediation of contaminants in a semi-controlled, relatively natural manner. The approach can be used potentially within a dissolved plume, IPTF, or within a source, ISTF, the latter is the more difficult to both scientifically and technically undertake. The site, VP12S, for which most local data have been obtained to date would appear to be in the ISTF category due to elevated naphthalene concentrations. Subject to the results of on-going assessment, it is proposed to install a TF at this location soon.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of MJCA, CL:AIRE and the assistance and research steering provided by the SIReN Board and Shell Global Solutions.

REFERENCES

Brown, M.J., McMaster, M.L., Barker, J.F., Devlin, J.F., Katic, D.J., and Froud, S.M. 1999. Passive and semi-passive techniques for groundwater remediation. In: *Accelerated bioremediation using slow-release compounds. Selected Batelle conference papers 1993-1999*. Ed: Koenigsberg, S.S., Norris, R.D. Regenesis Bioremediation Products, San Clemente, CA.

Jones, D., Lethbridge, G., McCarthy, P., and Thomson, S. 2001. Project SIReN: Phase 2a Conceptual site model and groundwater model. R&D Technical Report P2-208/TR/2. Environment Agency, Bristol.

Leblanc, D.R., Garabedian, S.P., Hess, K.M., Gelhar, L.W., Quadri, R.D., Stollenwerk, K.G. and Wood, W.W., 1991. Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 1. Experimental design and observed tracer movement. Water Resour. Res. **27(5)**, 895-910.

Lethbridge, G., Scott, P., and Earle, R. 2003. Project SIReN: Phase 2b Further Investigation of the SIReN site. R&D Technical Report P2-208/TR/3. Environment Agency, Bristol.

MacIntyre, W.G., Boggs, M., Antworth, C.P., and Stauffer, T.B. 1993. Degradation kinetics of aromatic organic solutes introduced into a heterogeneous aquifer. Water Resour. Res. **29**, 4045-4051.

Mackay, D.M., Freyberg, D.L., Roberts, P.V., and Cherry, J.A. 1986. A natural gradient experiment on solute transport in a sand aquifer: 1. Approach and overview of plume movement. Water Resour. Res. **22 (13)**, 2017-2029.

Rivett, M.O., and Allen-King, R.M. 2003. A controlled field experiment on groundwater contamination by a multicomponent DNAPL: dissolved-plume retardation. J. Cont. Hydrol. **66**, 117-146.

Rivett, M.O., Feenstra, S., and Cherry, J.A. 2001. A controlled field experiment on groundwater contamination by a multicomponent DNAPL: creation of the emplaced-source and overview of dissolved plume development. J. of Cont. Hydrol. **49**, 111-149

Rügge, K., Bjerg, P.L., Pedersen, J.K., Mosbæk, H., and Christensen, T.H. 1999. An anaerobic field injection experiment in a landfill leachate plume (Grinsted, Denmark): 1. Experimental set-up, tracer movment and fate of aromatic and chlorinated compounds. Water Resour. Res. **35**, 1231-1246.

Thierrin, J., Davis, G.B. and Barber, C. 1995. A groundwater tracer test with deuterated compounds for monitoring in situ biodegradation and remediation of aromatic compounds. Ground Water **33(3)**, 469-475.

Biographical Note

Mr Richard Croft

Richard is the Managing Director of RemedX Ltd who are a specialist soil and groundwater remediation contractor. He first began work in contaminated land in 1993 for Komex International. Prior to this his first degree was in Mining Engineering from the University of Nottingham, after which he joined the Regular Army and was commissioned in the Royal Engineers. On leaving the Army he completed a Masters at Imperial College in Hydrology. On joining Komex he worked in Canada and the USA primarily in assessment and remediation of sites used in the upstream and downstream sides of the oil and gas industry. Specific experience was gained in using in-situ remediation techniques. He returned to the UK in 1995, where he focussed on the investigation and remediation of gasworks sites. He founded RemedX in the UK in 1998.

Mr Paul Noble

Paul Noble leads the contaminated land management capability in ABB Engineering Services. He is a senior environmental consultant with ten years experience of assessment of potentially contaminated sites, remedial options appraisal and site remediation, due diligence assessment, site closure and redevelopment and environmental liability identification and management.

CL:AIRE Technical Demonstration Project (TDP) 16:

Ex-*situ* soil vapour extraction to remediate chlorinated hydrocarbons

Richard Croft, RemedX Ltd

Paul Noble, ABB Engineering Services

CL:AIRE Annual Project Conference,
20 April 2004

Contents

- CL:AIRE TDP 16 Objectives
- Background
- Health & Safety Requirements
- Remediation Design
- SVE System Design
- Excavation Operation
- Closeout
- Air Dispersion Modelling
- Mass Balance
- Lessons Learned

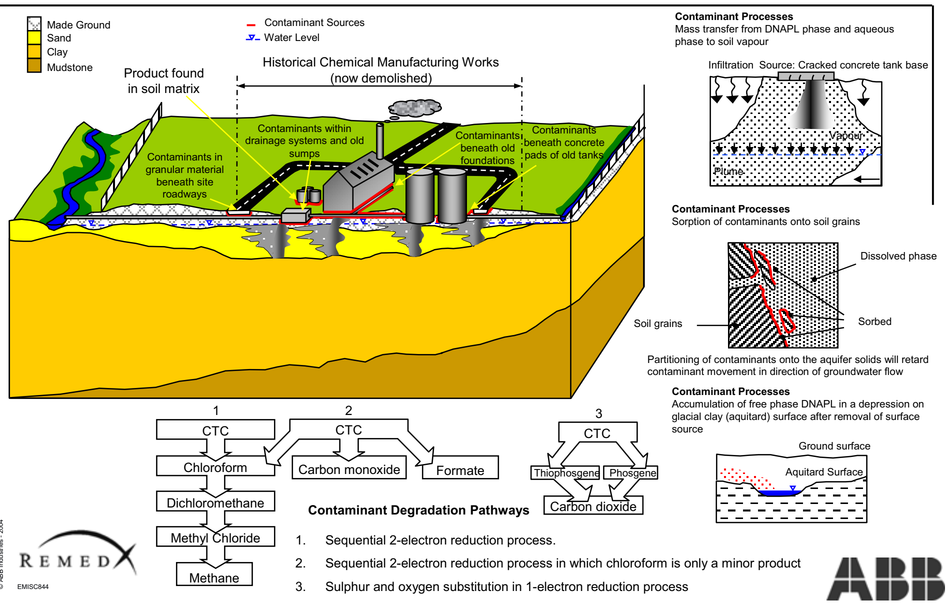
CL:AIRE Technical Demonstration Project (TDP) 16

- An assessment of the performance of ex-situ soil vapour extraction in above ground treatment beds.
- An assessment of the health and safety risks of excavation and treatment of chlorinated hydrocarbon contaminated soils along with a discussion of associated air monitoring requirements.
- An assessment of the feasibility and uncertainties of a mass balance on volatilisation losses during excavation and treatment.

Background (1)

- Conceptual Site Model
- Purpose and Objectives of Overall Project
  - Voluntary Remediation
  - Controlled Waters
  - Human Health
  - <6 Months duration
- Remediation Options Appraisal

Conceptual Site Model and Generalised Contaminant Processes



Contaminant Processes
Mass transfer from DNAPL phase and aqueous phase to soil vapour

Contaminant Processes
Sorption of contaminants onto soil grains

Partitioning of contaminants onto the aquifer solids will retard contaminant movement in direction of groundwater flow

Contaminant Processes
Accumulation of free phase DNAPL in a depression on glacial clay (aquitard) surface after removal of surface source

Contaminant Degradation Pathways

1. Sequential 2-electron reduction process.
2. Sequential 2-electron reduction process in which chloroform is only a minor product
3. Sulphur and oxygen substitution in 1-electron reduction process

---

Background (2)

- In-situ SVE Pilot Test
- Ex-situ SVE selection
- Legislation
  - Mobile Plant Licence
  - Waste Management Licence Exemption
  - Planning Permission
  - Duty of Care
- Development of cleanup criteria
- Delineation of remediation volume

Health and Safety

- Control of exposures to site workers and off-site residents:
  - Workplace monitoring: Excavation face, Treatment bed and Work Area Threshold Limit
  - Boundary monitoring
  - Fixed monitoring
- CDM Requirements – Full time health & safety works management
- Formal inductions and regular tool box talks and safety audits
- PPE including respiratory protective equipment

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ABB

In situ SVE Pilot Testing

- THREE SVE EXTRACTION WELLS WITHIN AN ARRAY OF VAPOUR MONITORING WELLS
- ALL LOCATED WITHIN THE DELINEATED CTC SOIL CONTAMINATION ZONE
- FOUR SVE TESTS PERFORMED EACH 24 HOURS LONG
- PARAMETERS DETERMINED:
  - Radii of influence
  - Mass recovery rates and any trend
  - vacuum/flow characteristics of the vadose zone

REMEDX

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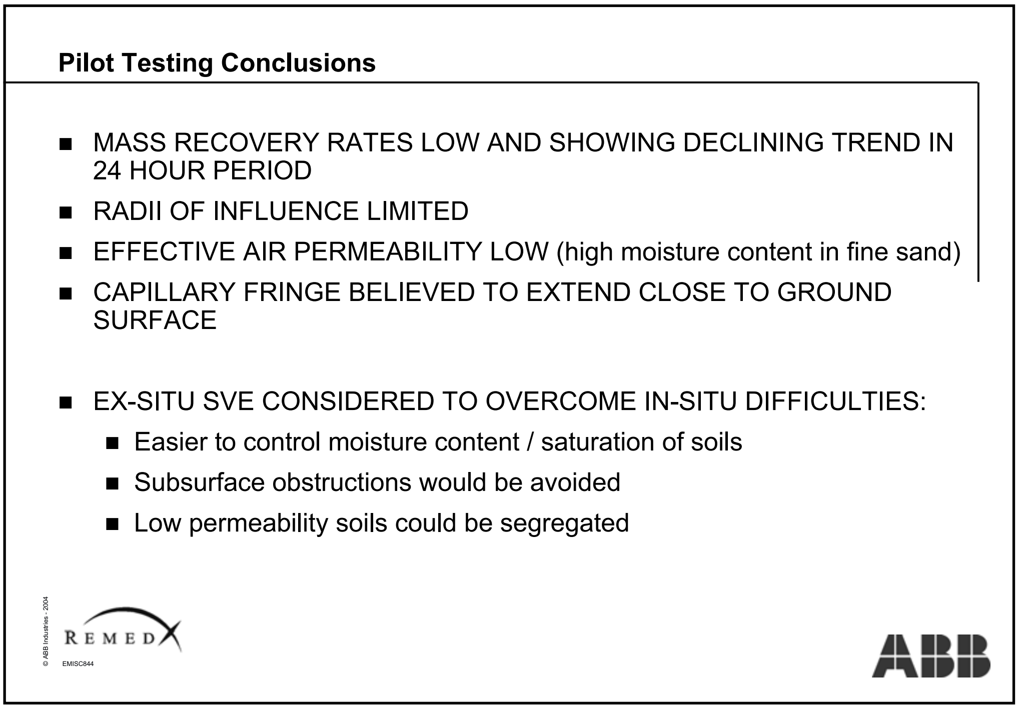

Pilot Testing Conclusions

- MASS RECOVERY RATES LOW AND SHOWING DECLINING TREND IN 24 HOUR PERIOD
- RADII OF INFLUENCE LIMITED
- EFFECTIVE AIR PERMEABILITY LOW (high moisture content in fine sand)
- CAPILLARY FRINGE BELIEVED TO EXTEND CLOSE TO GROUND SURFACE

- EX-SITU SVE CONSIDERED TO OVERCOME IN-SITU DIFFICULTIES:
  - Easier to control moisture content / saturation of soils
  - Subsurface obstructions would be avoided
  - Low permeability soils could be segregated

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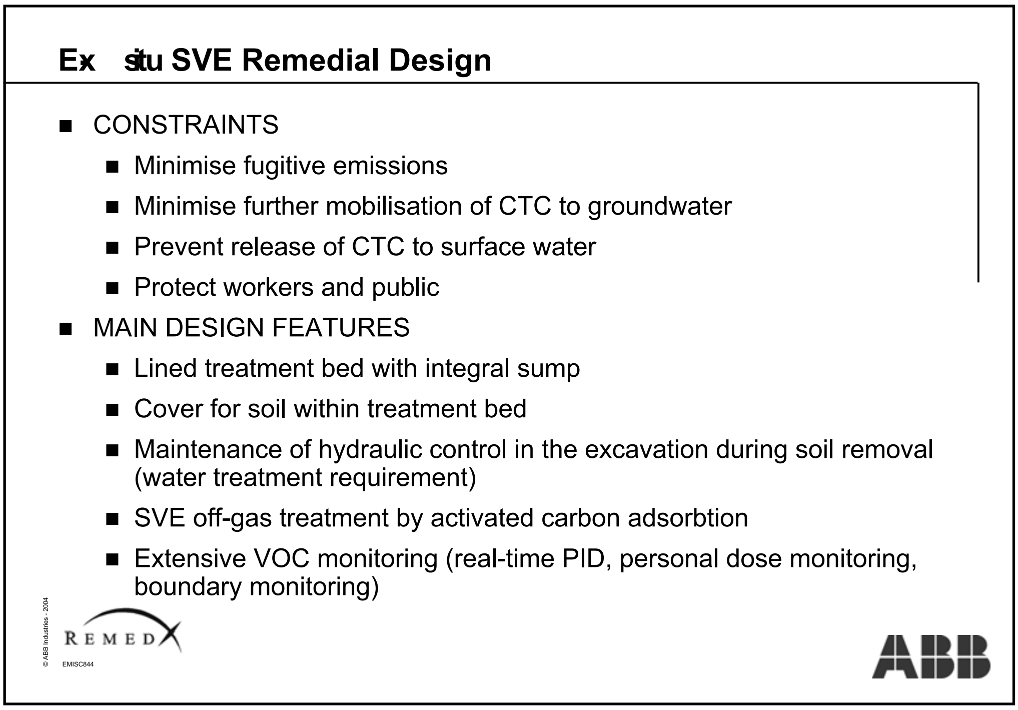

Ex situ SVE Remedial Design

- CONSTRAINTS
  - Minimise fugitive emissions
  - Minimise further mobilisation of CTC to groundwater
  - Prevent release of CTC to surface water
  - Protect workers and public
- MAIN DESIGN FEATURES
  - Lined treatment bed with integral sump
  - Cover for soil within treatment bed
  - Maintenance of hydraulic control in the excavation during soil removal (water treatment requirement)
  - SVE off-gas treatment by activated carbon adsorbtion
  - Extensive VOC monitoring (real-time PID, personal dose monitoring, boundary monitoring)

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Construction of Treatment Bed

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Covered Treatment Bed

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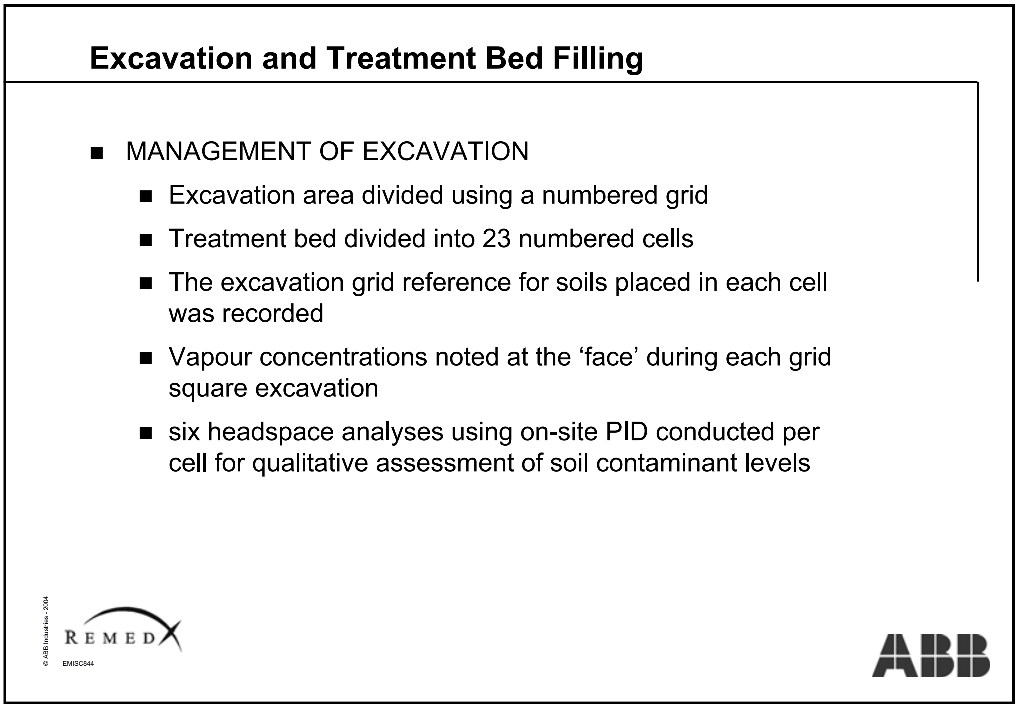
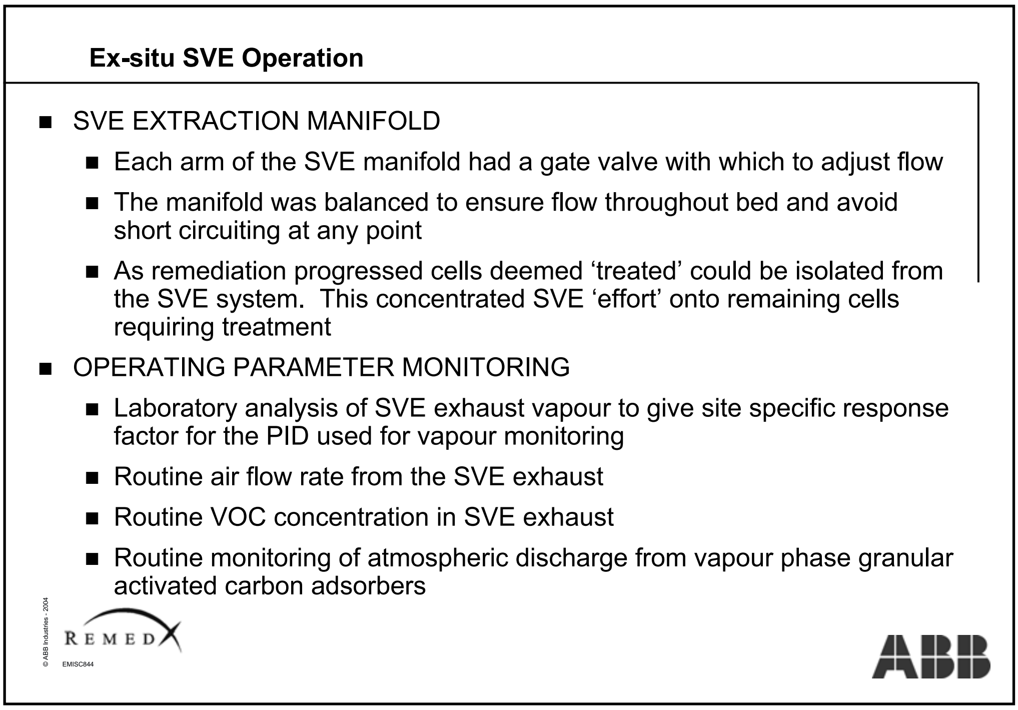


Excavation and Treatment Bed Filling

- MANAGEMENT OF EXCAVATION
  - Excavation area divided using a numbered grid
  - Treatment bed divided into 23 numbered cells
  - The excavation grid reference for soils placed in each cell was recorded
  - Vapour concentrations noted at the 'face' during each grid square excavation
  - six headspace analyses using on-site PID conducted per cell for qualitative assessment of soil contaminant levels



Ex-situ SVE Operation

- SVE EXTRACTION MANIFOLD
  - Each arm of the SVE manifold had a gate valve with which to adjust flow
  - The manifold was balanced to ensure flow throughout bed and avoid short circuiting at any point
  - As remediation progressed cells deemed 'treated' could be isolated from the SVE system. This concentrated SVE 'effort' onto remaining cells requiring treatment
- OPERATING PARAMETER MONITORING
  - Laboratory analysis of SVE exhaust vapour to give site specific response factor for the PID used for vapour monitoring
  - Routine air flow rate from the SVE exhaust
  - Routine VOC concentration in SVE exhaust
  - Routine monitoring of atmospheric discharge from vapour phase granular activated carbon adsorbers

Assessment of SVE Performance

- ON-GOING MASS RECOVERY CALCULATIONS
  - The vapour flow rate and VOC monitoring were used to estimate VOC mass recovery rates
  - From the mass recovery rates a cumulative VOC mass recovery was calculated
- ESTIMATING SOIL CONTAMINANT LEVELS DURING OPERATION
  - Periodic sampling of treatment bed and use of on site PID for headspace testing.
  - Each treatment bed cell verified by laboratory analysis of a duplicate samples selected from the highest PID headspace test
  - Continued treatment of cells not below site specific target levels

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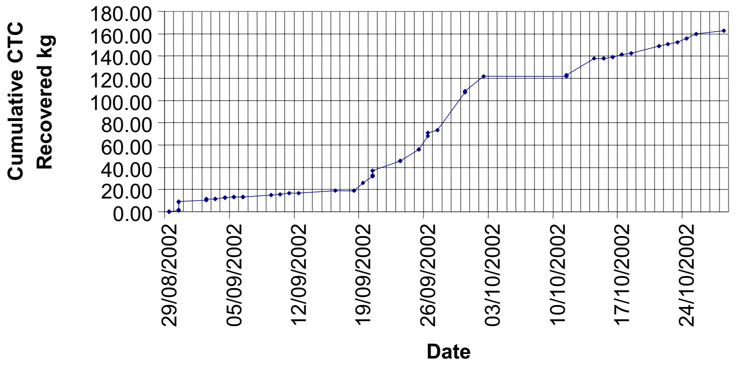
Cumulative Mass Recovery

First Treatment Bed Fill



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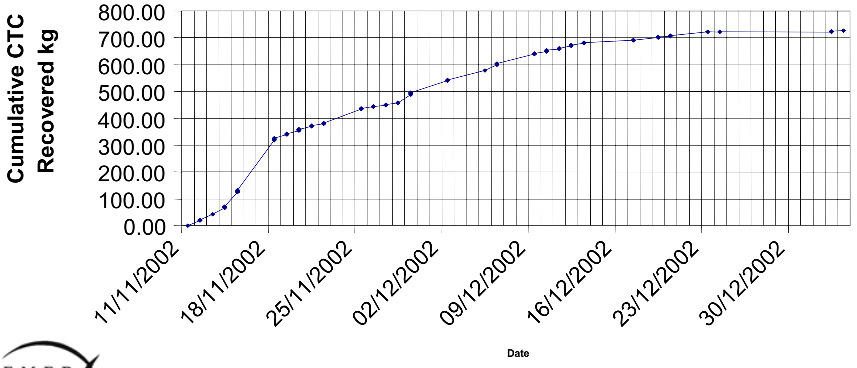
Cumulative Mass Recovery

Second Treatment Bed Fill



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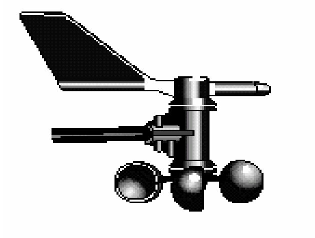
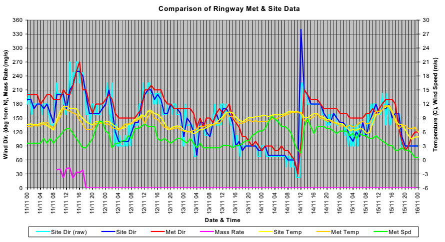
Atmospheric monitoring

- Site weather station monitored
  - Wind speed
  - Wind direction
  - Temperature
- Local Met Office monitored
  - All of the above
  - Atmospheric turbulence (Monin-Obukov length)
- Concentration monitoring
  - Passive diffusion tubes
  - Personnel & soil samples





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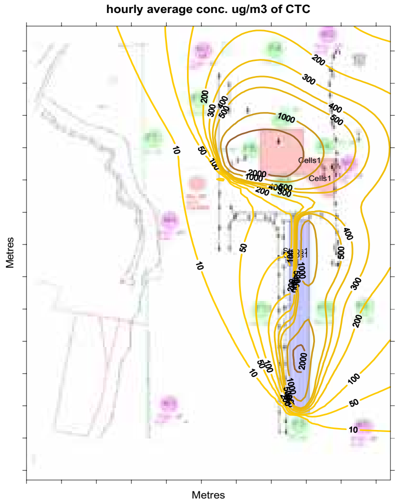
Air dispersion analysis

- Data for 5 weeks during excavations
- ‘Source terms’ back calculated based on:
  - Hourly wind-weather data
  - Location of activity (6 areas)
  - Activity - number of cells dug
  - ‘Base’ soil loading factor
- Iterative solution for ‘best fit’ to monitor data
- Total mass emissions estimated from summed source terms



Mass Balance

- Mass of VOCs present in remediation volume prior to start of project
- Mass of VOCs collected by SVE treatment system
- Mass of VOCs estimated to have been emitted to atmosphere from boundary monitoring data and ADMS
- Mass present in backfilled material (below site specific cleanup criteria)

Lessons Learned

- Site Investigation Data
- Legislation:
  - Early discussion with authorities
  - Importance of good relations with authorities
  - Importance of good relations and communication with local community
- Disposal of treated water
- Health & Safety Management

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Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

Ex-Situ Soil Vapour Extraction To Remediate Chlorinated Hydrocarbons

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INTRODUCTION

Organic chemical manufacture was carried out at the project site from the 1940s to the 1990s. Carbon tetrachloride (CTC), together with chloroform (an impurity of the CTC) was used in this operation and released to ground during the lifetime of the plant. Ground conditions at the site comprise made ground (variable depths but average occurrence 0-0.5m of hardcore, pipe trenches, submerged concrete structures with associated viscous organic product containing chlorinated hydrocarbons) overlying a medium sand (average 0.5 – 2.0m), which in turn, overlies a stiff clay (>2.0m). Remediation was proposed in order to prevent CTC from contaminating a local stream and leave the area suitable for commercial end-use.

A volume of approximately 2,500m^3 (which included the highest concentrations of chlorinated organics detected by previous investigations) was defined as requiring remediation by investigations with reference to site-specific cleanup goals. The area covered by this soil volume coincided with the location of the former carbon tetrachloride (CTC) storage tanks.

Soils data for the former CTC tankage area were analysed in order to estimate the mass of total volatile organic compounds (VOCs) present in the remediation volume prior to remediation. The data were manipulated in a number of different ways in order to give an indication of the likely range of VOC mass present. The impacted area was divided into two layers (upper and lower) in a grid pattern to give two sets (layers) of cells of discrete volume. The average concentration of each cell was calculated using the available site investigation data to allow computation of the estimated mass in each cell (assuming that this average concentration was representative of all the soil in that cell).

SELECTION OF REMEDIATION METHOD

The following remediation options were assessed:

1. Excavate and dispose to landfill, however, cost estimates were high and there was uncertainty about availability of landfill to take these types of waste;
2. Capping - was considered unlikely to achieve the remedial objectives;
3. Soil Vapour Extraction - appeared to be the most cost-effective potential approach;
4. Bioremediation - likely to require a number of years to implement;
5. Thermal desorption - was considered better suited to much larger volumes of soil and also likely to be relatively expensive for the volumes of soil concerned.

Hence, soil vapour extraction (SVE) was considered to be a viable option for CTC removal and a pilot trial for in-situ SVE was carried out. This trial indicated that SVE could be successful, but that the ground conditions were not conducive to in-situ treatment and an ex-situ scheme was proposed.

Soil vapour extraction is a remediation technique that is commonly used to physically remove volatile compounds from contaminated soils above the water table (vadose zone). The process involves recovering soil gas from the vadose zone by applying vacuum at selected points within the contaminated zone. The process relies totally on the partitioning of volatile contaminants into the vapour phase, and thus into the soil gas present within the soil pore spaces.

COMPARISON OF IN-SITU AND EX-SITU SVE RELATIVE TO THE PROJECT SITE

The following section summarises pros and cons of In-Situ SVE and Ex-Situ SVE with specific reference to the project site.

Advantages of In-situ SVE:

- Excavation/abstraction of contaminated soil/water, if required to meet the remedial objectives, would take place at lower contaminant concentrations;
- Lower emissions to atmosphere.

Advantages of Ex-situ SVE:

- Can deal with variations in contaminant concentrations (e.g. viscous product observed in discrete zones at the site)
- Can deal with variations in grain size and nature of material
- Shorter time of operation (12 weeks per treatment bed in-fill)
- Higher degree of confidence in attaining cleanup target
- Ease of sampling to check progress
- Moisture content can be controlled

Disadvantages of In-Situ SVE:

- Potentially longer period of operation
- More uncertainty as to final cleanup target
- Problem of dead zones due to heterogeneity

Disadvantages of Ex-situ SVE:

- Air emissions during excavation

Hence, the principal benefits of this project were:

- Cost-effective remediation when compared to other options;
- Time-efficient remediation when compared to other options given the project aim which was to reduce concentrations of VOCs in surface water drainage and remediate soils such that site specific cleanup criteria are met in a timeframe of 6 months or less;
- Reduction in amount of waste transported off-site for disposal - this method was considered to have wider environmental benefits linked to reducing traffic movements and producing less waste for landfill disposal
- Ex-situ option should ensure that contamination in awkward areas (e.g. within redundant process drains, clay pockets, former concrete structures, e.t.c.) is identified and treated.

LEGISLATION

Details of liaison with statutory authorities are summarised below:

Item:	**Statutory Authority:**	**Description:**
Mobile Plant Licence	Environment Agency – Environmental Protection	RemedX Ltd activated their mobile plant licence by producing a Site Specific Working Plan and Site Specific Risk Assessment, which were agreed with the EA. Approval was conditional upon implementation of a surface and groundwater monitoring programme and agreement of site specific cleanup criteria
Planning Permission	Vale Royal Borough Council	Planning Permission was obtained to undertake the remediation project. This included measures to be

		taken to protect the public from nuisance (e.g. noise, odours)
Waste Management Licence Exemption	Environment Agency – Waste Regulation	A waste management licence exemption was granted covering replacement (backfill) of treated soils
Waste Disposal	Environment Agency – Waste Regulation	Duty of Care

EX-SITU SVE REMEDIATION SCHEME

The remediation methodology is summarised in the following steps:

1) Excavation of contaminated soils;
2) Validation of soil quality in excavation sides and base;
3) Abstraction of water and treatment;
4) Construction of treatment bed;
5) Treatment bed filling;
6) Operation of the treatment bed;
7) SVE Plant Operation and continuous assessment of treatment bed performance;
8) Validation of soil treatment results (i.e. monitoring of contaminant concentrations in treatment bed);
9) Backfill of treated soils into original excavation.

Detailed work plans were developed for:

- Vapour Control of Excavation of Volatile Organic Compound Contaminated Soils Such That Vapour emissions do not exceed action levels;

- Excavation of VOC Contaminated Soils from the Former Tankage Area including Delineation, Redundant Drainage Removal, Redundant Structure Removal, Soil Excavation Sequencing, Residual Soil Quality Validation, Reinstatement.

- Treatment Bed Construction, Filling Sequence, Bed Turning, Plant Operation, Controls, Monitoring, Soil Quality Validation, Carbon Management.

Real-time VOC monitoring was specified to provide a practically workable and safe method for protecting workers and measuring exposures at the excavation, treatment bed, site boundary and at a fixed point to the nearest residential properties. Monitoring at the excavation and treatment bed was designed to detect peak concentrations which could cause ill-health effects as a result of acute exposures.

A guide to preventing exposures from exceeding the eight-hour time-weighted average (TWA) of 2 ppm of VOCs was achieved using the above real time monitoring. Exceeding the TWA of 2 ppm would require an exposure to an average of 20ppm for the individual (due to the safety factor of the Respiratory Protective Equipment of 10).

In order to provide retrospective confirmation data, site personnel (3 plant operators, 2 environmental scientists) wore carbon tubes with pumps in order to measure average daily exposure. A percentage of the tubes were analysed with 3-5 day turnaround to provide confirmation.

Measures to reduce VOC emissions during operation were:

- Reduce excavation rate, use smaller buckets for areas with higher concentrations of contaminant, excavate more slowly;
- Reduce exposed contaminated soils – uncontaminated soils were available to cover more contaminated areas.

- Leave contaminated areas covered at the end of each working day;
- Transport excavated soils rapidly to treatment bed and cover.

Once an area was excavated, the soil quality in the base and sides of that part of the excavation was sampled and analysed. This was done at the end of excavation by collecting samples 0.3-0.5m into the sides or base (to ensure a fresh sample was collected). One half of each sample was head-space tested on site using a PID. The second half of each sample will be sent to a chemical testing laboratory for analysis.

If the laboratory results are below the Site Specific Cleanup Levels, then the excavation limits tested were deemed the excavation's final extent. If the laboratory analysis results showed values above the Site Specific Cleanup Levels, then further excavation was required.

The ex-situ soil vapour extraction bed was designed with the following features:

- to ensure segregation of the contaminated soil from the clean ground, and to prevent leachate or free draining liquids infiltrating into the ground beneath.
- to have sufficient liquid storage capacity to be able to capture precipitation falling within the bed such that this can be pumped out periodically to a treatment plant prior to disposal.
- to contain vapour extraction pipe network such that soil vapours within the contaminated soils are readily recovered by applying a vacuum to the network.
- to be robust enough to be filled and emptied repeatedly by heavy earthmoving plant such that the bed is not destroyed during these activities.
- to minimise the fugitive emissions of VOC to the atmosphere from the bed, achieved by covering the soils in the bed during operation with high density plastic sheeting.

The vapour extraction plant's purpose was to extract vapour from the treatment bed soils by applying a vacuum to the venting pipe work manifold. Vapour is drawn into the manifold under vacuum and is then discharged from the vacuum pumps through a discharge manifold into two granular activated carbon vessels mounted in series.

The plant was capable of flexible operation using multiple vacuum pumps. This allowed the applied vacuum and flow rate to be varied depending on the vapour extraction requirements at the time. The plant operating parameters of vacuum, flow rate, VOC vapour concentration and temperature were monitored using hand held instruments.

Sampling of the treatment cells within the treatment bed took place periodically during treatment using the headspace technique. Validation sampling took place after a number of weeks of treatment bed operation. On the basis of the validation sampling, the contents of forty treatment cells were backfilled, the contents of two cells were treated through two phases of treatment while the contents of one cell was disposed of to landfill. This equates to a total volume of approximately 1,000 m^3 of (sandy) soil (measured by volume in ground), which was treated to concentrations below the cleanup criteria, and therefore backfilled.

Mass Balance

A VOC mass balance estimate is in preparation with the following parameters approximated:

- mass of contaminants present in remediation area at outset (M_o),
- mass of contaminants emitted to atmosphere derived from extensive boundary and personal monitoring, weather data and air dispersion modelling (M_b). Personal and vapour monitoring points were situated at distances of 0-200m from the excavation and treatment areas. Most emissions are likely to have occurred during excavation, treatment bed filling and treatment bed turning
- mass of contaminants present in activated carbon after treatment (M_c),
- mass of contaminants collected by treatment system by measuring concentration passing through total discharge air flow (M_d),

- mass present in treatment bed after treatment (M_t).

This mass balance for the soils aspect of the remediation is represented by the following equation:

$$M_o = (M_c \text{ or } M_d) + M_b + M_t$$

Volatile loss to atmosphere has been estimated using ADMS Version 3.1 to 'back calculate' the source term (i.e. emission rate) on the basis of the following site-specific data:

- on-site weather station output supplemented by regional weather station records;
- site log describing type and duration of activities on site;
- VOC concentration data from diffusion carbon tubes on the site boundary, worker-mounted pumped samples and selected instantaneous breathing zone monitoring using a PID.

It was considered that ADMS is an appropriate model to use for this exercise as it is designed to deal with relatively low concentrations typical of environmental projects. A degree of uncertainty is accepted when estimating the source term in this way due to the very nature of excavating contaminated soils and the number of controlling factors (initial contaminant distribution in the ground, properties of soil, degree of disturbance during excavation and transport to the treatment bed, weather conditions, etc). This uncertainty will be included in the final mass balance results.

Conclusions

All treated material required successful validation testing prior to backfill. Concentrations in each treatment cell were below site-specific cleanup criteria, with the exception of 1 treatment cell out of 40 cells, which did not meet the site-specific cleanup criteria and was dispatched to landfill under duty of care regulations. Validation sampling of the base and sides of the excavation void prior to backfill was carried out during the project - results indicated that the SSCVs were achieved.

Whilst it was attempted to limit the mass of soils disposed of to landfill, the following material was disposed in this way:

- soil unsuitable for treatment (mainly clay and made ground);

- viscous product containing CTC;

- vapour phase granular activated carbon used for treatment of the vapour discharge from the soil vacuum extraction plant;

- liquid phase granular activated carbon used for treatment of water from dewatering of the excavation and the treatment bed.

Given that the project was competed in 6 months, the project achieved the stated contract objectives. In addition, there were no health and safety incidents or complaints from the public.

Conclusions with regards to the success of ex-situ soil vapour extraction and the feasibility of a mass balance will be presented in the TDP report which is in preparation.

Biographical Note

Mr Michael Brown

Mr Michael Brown is a Research Associate at the University of Sheffield. He is a member of the Department of Civil and Structural Engineering's Groundwater Protection and Restoration Group and currently manages the SUBR:IM project. After his first degree in Civil and Structural Engineering at the University of Bradford, he worked for 4 years with different geotechnically based contractor and consultants, specialising in tunnel engineering. Michael returned to university in 1999 as a member of the Geotechics Research Group and registered for a part time PhD investigating "The rapid load testing of piles in clays". By the time of this conference he will have submitted his thesis and will be finding out what spare time means.

Dr Colin Smith

Dr Colin Smith is a lecturer at the University of Sheffield whose research encompasses three broad themes; fluid, contaminant and thermal transfer processes in the ground, sorption and leaching of contaminants in soils, and performance of landfill liners and low permeability soils. After his first degree at the University of Cambridge he joined the Cambridge Soil Mechanics research group and completed his PhD on "The centrifugal modelling of heat transfer and pipeline settlement". Following 2 years as a Research Associate at Cambridge he was appointed as a lecturer in Geotechnics at Sheffield. In his spare time he enjoys orienteering.

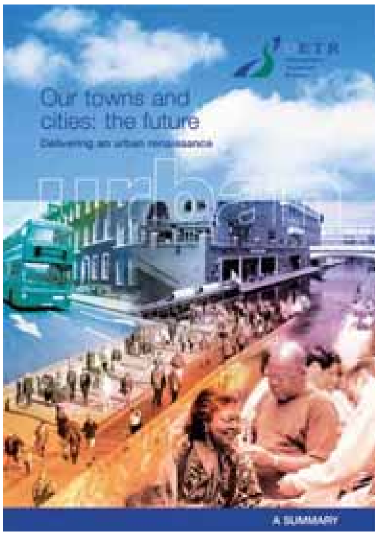
SUBR:IM

Restoration of Acid Tar Lagoons: SUBR:IM Work Package H

Presented by Michael Brown & Colin Smith,
University of Sheffield,
www.subrim.org.uk

The Problem

- Urban regeneration can only be achieved by using Brownfield land.
- Up to 10% of the land in some cities is classed as derelict.
- High remediation costs but low development value.
- Complex obstacles such as contamination.



The Problem

- Urban regeneration can only be achieved by using Brownfield land.
- Up to 10% of the land in some cities is classed as derelict.
- High remediation costs but low development value.
- Complex obstacles such as contamination.

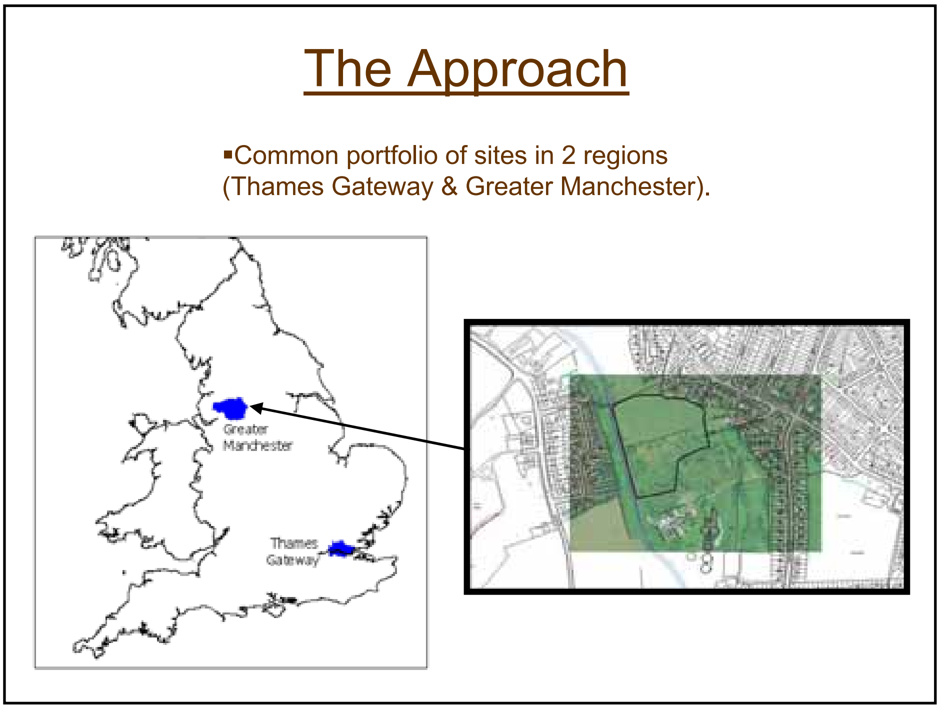
SUBR:IM - Aims and Objectives

AIM

- Produce integrated & sustainable solutions.

OBJECTIVES:

- Enhance technical solutions and tools for restoration.
- Increase stakeholder knowledge & integrate needs within a sustainable framework.
- Establish best environmental practice.



The Approach

- Common portfolio of sites in 2 regions (Thames Gateway & Greater Manchester).

The Approach

- Multi-disciplinary approach with:
  - 9 Research organisations
  - 23 Collaborating organisations
  - Stakeholder led steering group

Research organisations:

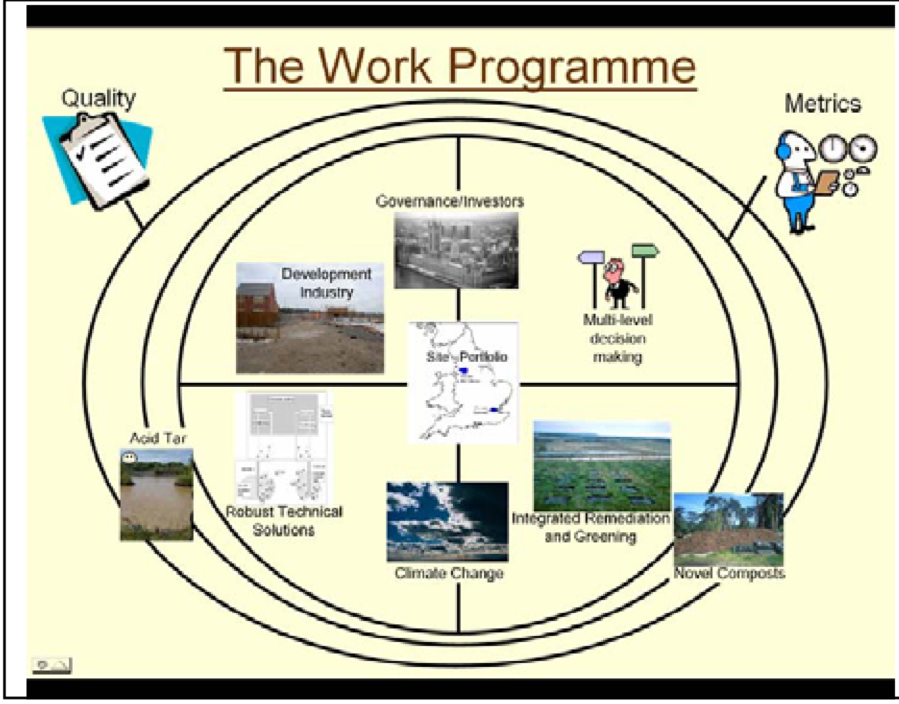
The Approach

- Multi-disciplinary approach with:
  - 9 Research organisations
  - 23 Collaborating organisations
  - Stakeholder led steering group

Collaborators:

The London Borough of Barking & Dagenham
The Mersey Forest
Environment Agency
CL:AIRE
Lattice
BPF
Office of the Deputy Prime Minister
RICS Foundation
Thames Gateway London Partnership

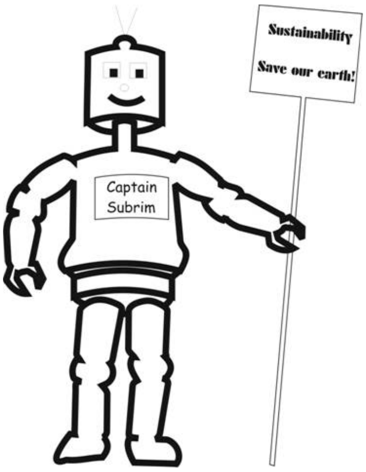
The Work Programme



Who Benefits

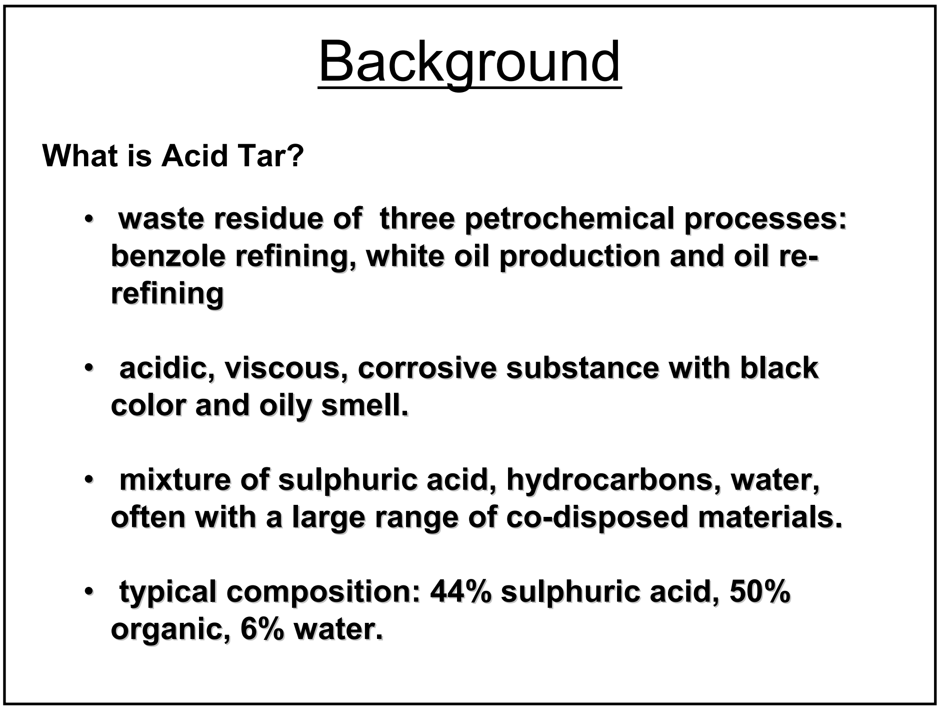
- Policy makers.
- Public.
- Agencies and Local Authorities
- Scientists and Social Scientists
- Landowners, their Advisors and Contractors

Special Guest



Restoration of Acid Tar Lagoons: SUBR:IM Work Package H

Colin Smith
University of Sheffield



Background

What is Acid Tar?

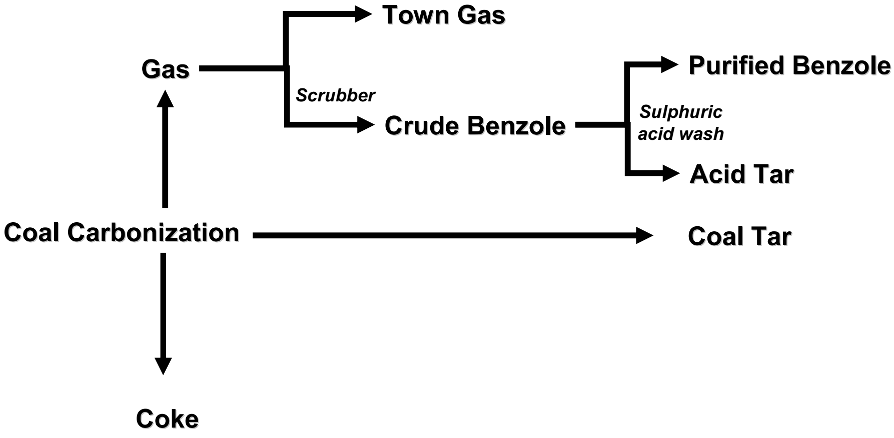
- **waste residue of three petrochemical processes: benzole refining, white oil production and oil re-refining**
- **acidic, viscous, corrosive substance with black color and oily smell.**
- **mixture of sulphuric acid, hydrocarbons, water, often with a large range of co-disposed materials.**
- **typical composition: 44% sulphuric acid, 50% organic, 6% water.**

Background

What is Acid Tar?

Background

Acid Tar Vs. Coal Tar



Town Gas

Gas

Scrubber

Crude Benzole

Purified Benzole

Sulphuric acid wash

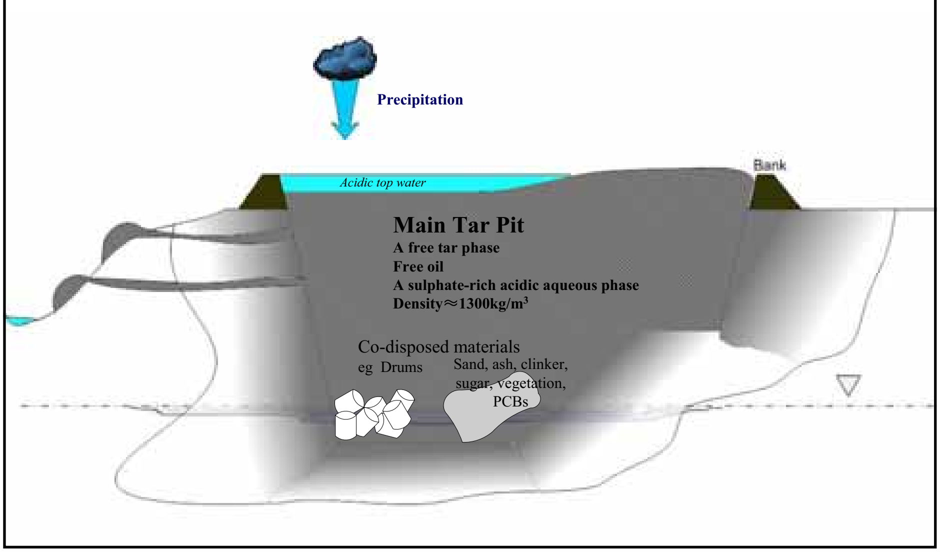
Acid Tar

Coal Carbonization

Coal Tar

Coke

Conceptual model

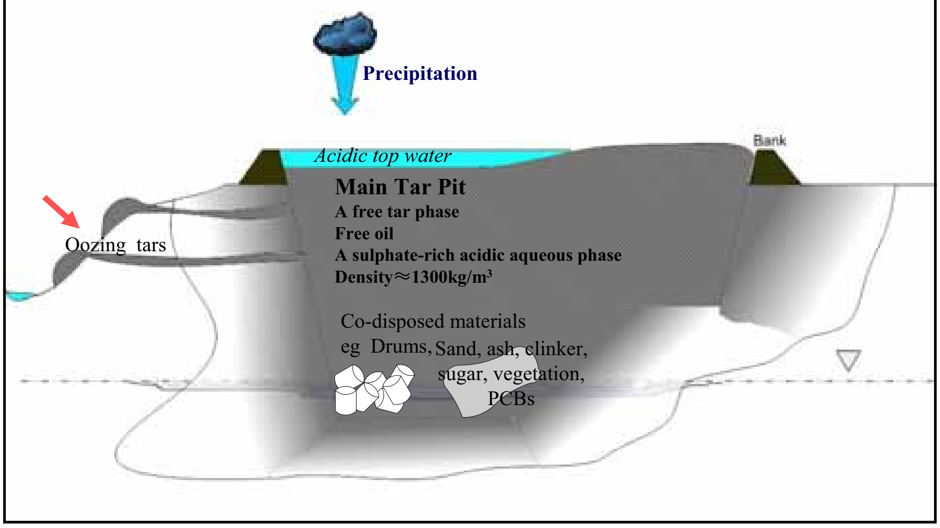


Main Tar Pit
A free tar phase
Free oil
A sulphate-rich acidic aqueous phase
Density≈1300kg/m^3

Conceptual model

Acidic Top Water

Conceptual model



Precipitation

Acidic top water

Bank

Oozing tars

Main Tar Pit

A free tar phase

Free oil

A sulphate-rich acidic aqueous phase

Density≈1300kg/m^3

Co-disposed materials

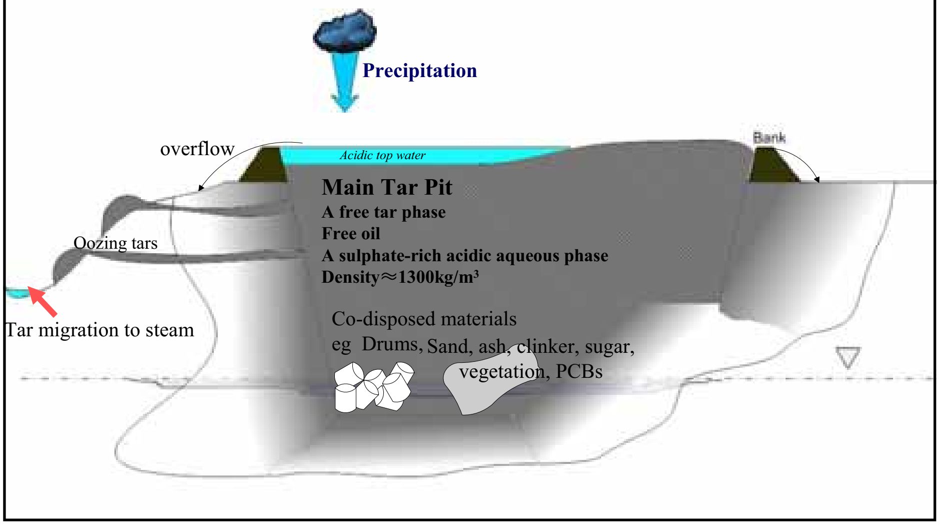
eg Drums, Sand, ash, clinker, sugar, vegetation, PCBs

Conceptual model

Oozing Tars

Conceptual model

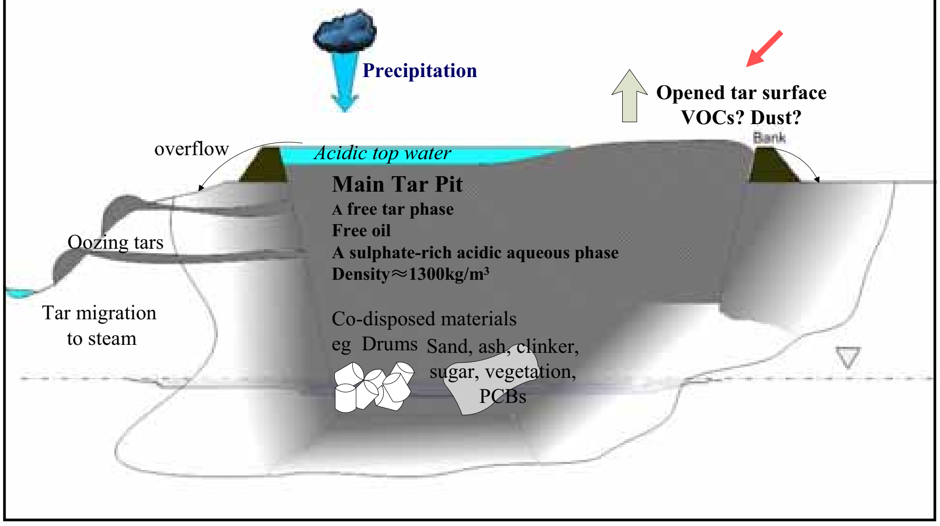
Conceptual model



Conceptual model

Tar migration near steam

Conceptual model



Precipitation

Opened tar surface
VOCs? Dust?

Bank

overflow

Acidic top water

Main Tar Pit
A free tar phase
Free oil
A sulphate-rich acidic aqueous phase
Density≈1300kg/m³

Oozing tars

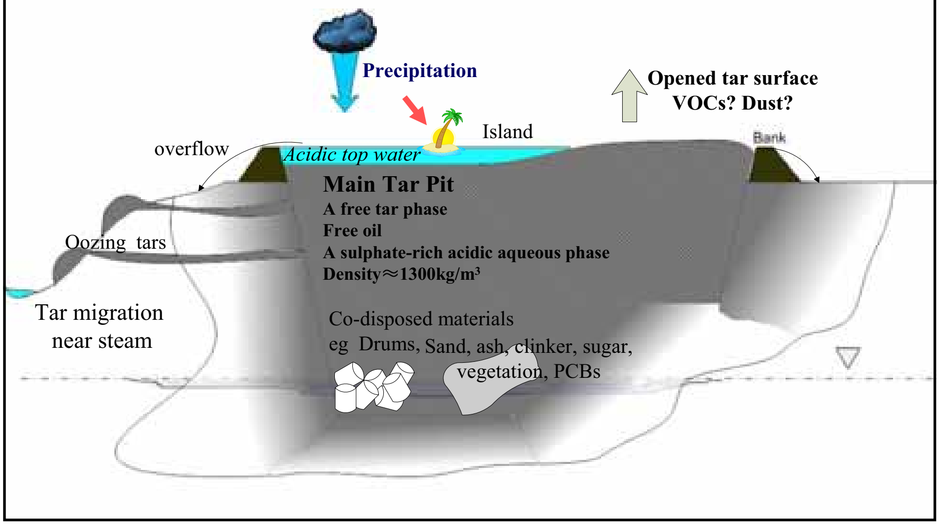
Tar migration
to steam

Co-disposed materials
eg Drums Sand, ash, clinker,
sugar, vegetation,
PCBs

Conceptual model

Opened tar surface

Conceptual model



Precipitation

Opened tar surface
VOCs? Dust?

Island

Bank

overflow

Acidic top water

Main Tar Pit
A free tar phase
Free oil
A sulphate-rich acidic aqueous phase
Density≈1300kg/m³

Oozing tars

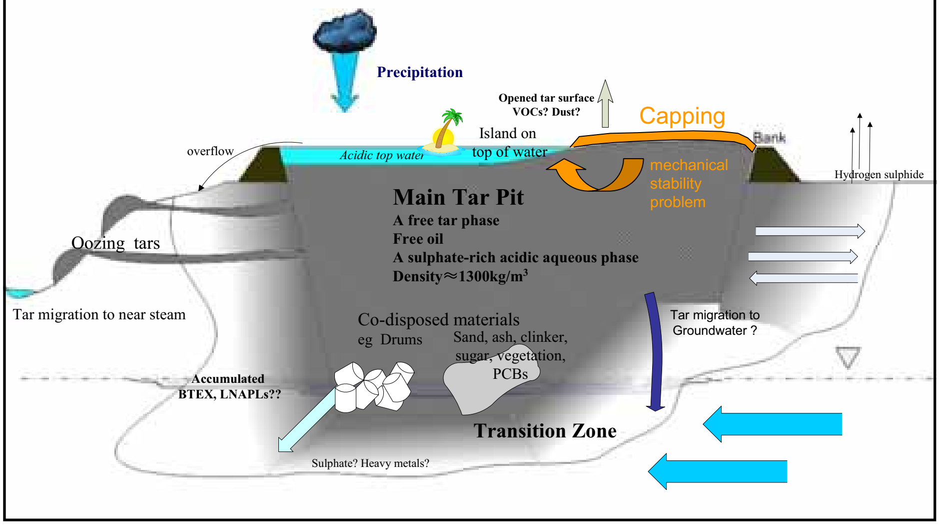
Tar migration
near steam

Co-disposed materials
eg Drums, Sand, ash, clinker, sugar,
vegetation, PCBs

Conceptual model

Island

Conceptual model



Conceptual model

Capping

Conceptual model

Capping

Key Linkages/Hazards

- Volatiles/gases
- Dust
- Leaching into ground / surface water
- Direct contact / ingestion
- Bulk migration
- Fire

Next steps

Site characterisation:

- Review of existing SI data
- Tar sampling – surface and shallow
- Soil sampling
- Surface water sampling
- Geophysics

Geophysics

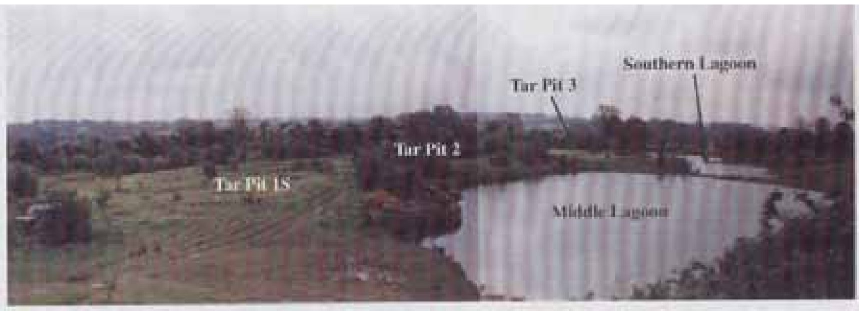
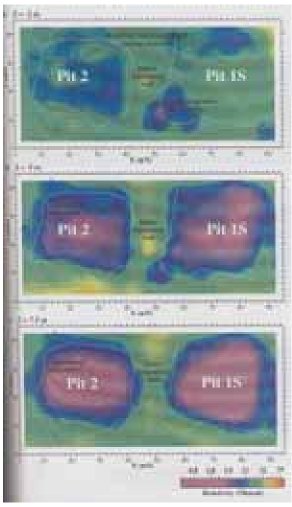
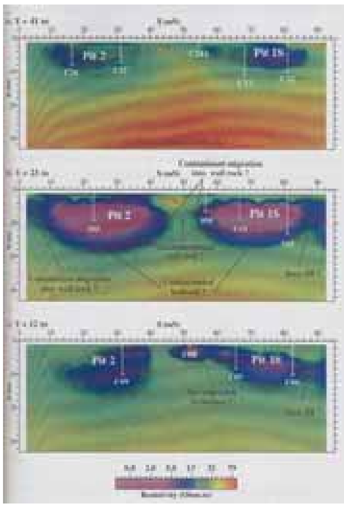


Figure 5.6. View of Survey Area 1, looking eastwards (May, 1999).

Chambers, J.E. (2001) PhD thesis, University of Sheffield

Geophysics





Chambers, J.E. (2001) PhD thesis, University of Sheffield

Next steps

Laboratory characterisation:

- Chemical/thermal analysis
- Leaching tests
- Mechanical properties
- Microbiology
- Weathering

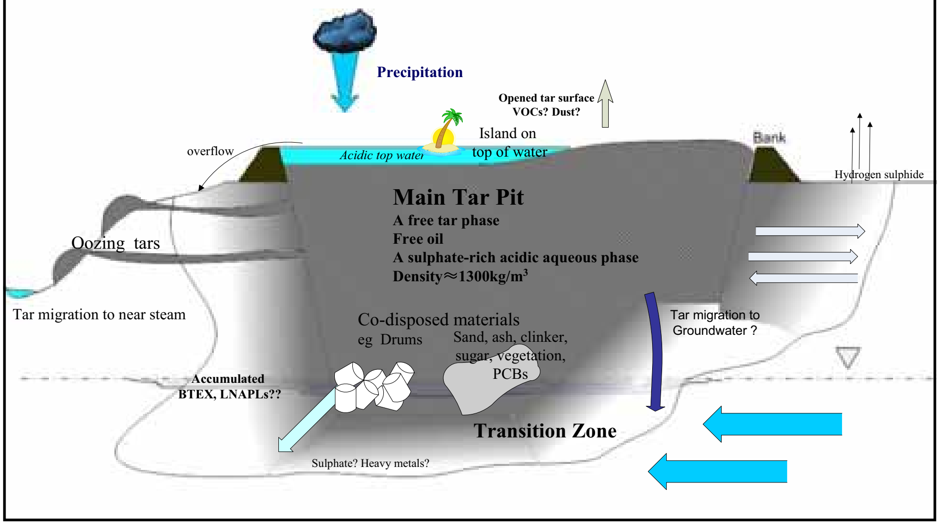
Remediation

- Containment: barrier stability
  - chemical compatibility
  - mechanical stability
- Natural attenuation
- Source control: incineration/stabilisation?
- Stakeholder views

Remediation

- Containment: barrier stability
    - chemical compatibility
    - mechanical stability
- Natural attenuation
- Source control: incineration/stabilisation?
- Stakeholder views

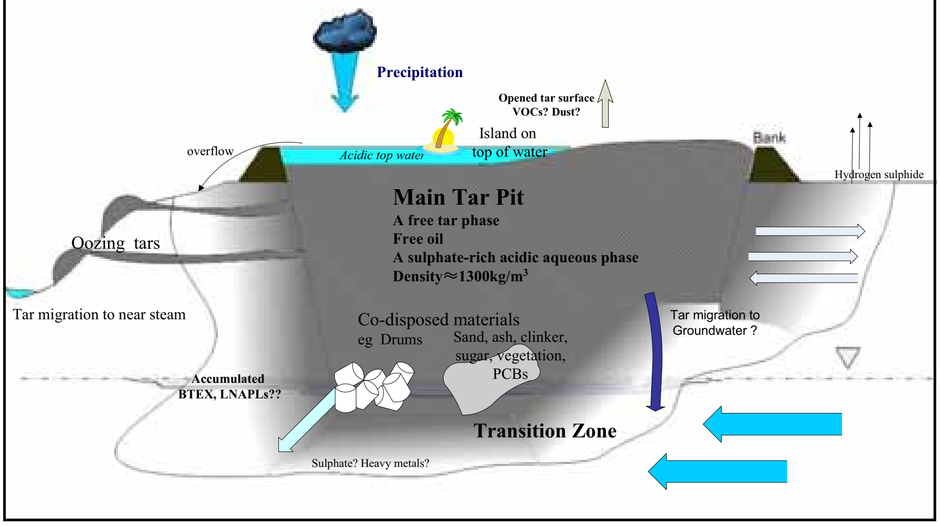
Remediation: barriers



Remediation

- Containment: barrier stability
  - chemical compatibility
  - mechanical stability
- Natural attenuation
- Source control: incineration/stabilisation?
- Stakeholder views

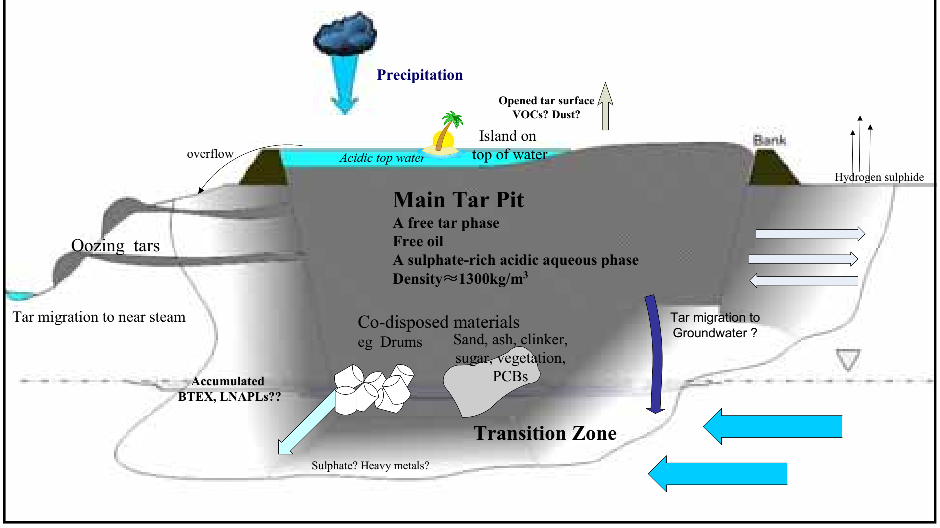
Remediation – natural attenuation



Remediation

- Containment: barrier stability
  - chemical compatibility
  - mechanical stability
- Natural attenuation
- Source control: incineration/stabilisation?
- Stakeholder views

Remediation: source control



Remediation

- Containment: barrier stability
  - chemical compatibility
  - mechanical stability
- Natural attenuation
- Source control: incineration/stabilisation?
- Stakeholder views

Data gathering and dissemination

- Currently in process of contacting owners of additional sites to build up database of SI and laboratory test data.
- Acid Tar Lagoons web site in process of being set up:
  - hosted at www.subrim.org.uk
  - will provide up to date bibliography, images, test data, abstracts
  - provides contact point for exchanges of data, establishment of links with other projects /remediations

End of presentation

Restoration of Acid Tar Lagoons: SUBR:IM Work Package H

Colin Smith[1], Xu Hao[2], Michael Brown[3]

[1]Lecturer, Research Student[2], Research Associate[3]
Department of Civil and Structural Engineering, University of Sheffield, UK

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ABSTRACT

Acid tar lagoons are a significant source of contamination that is a hazard to human health, controlled waters and the natural environment. Acid tars are normally defined as tars of high sulphuric acid content that have arisen as by-products of benzole refining, refining petroleum fractions (particularly white oil) and oil re-refining. In situ, acid tar comprises a mass of hydrocarbons that is generally viscous and tarry with very low pH. Surrounding soils are likely to be contaminated to varying degrees with tars and hydrocarbons. Many of these acid tar lagoons are now situated in close proximity to residential areas.

Due to the complexity of the problems associated with these sites, adequate, robust and durable long-term remediation options have not been developed. Previous attempts to break the pollutant linkage by capping sites have often failed technically due to the mobility of the tars. Excavation is environmentally unsustainable, while total encapsulation and destructive techniques are financially prohibitive.

INTRODUCTION

The research on the restoration of acid tar lagoons forms one work package (WP) of a large EPSRC funded research consortium: ‘Sustainable Urban Brownfield Regeneration: Integrated Management’ (SUBR:IM, www.subrim.org.uk). This consortium has initial funding of £1.9million to tackle the multidisciplinary research problems associated with brownfield land. As well as acid tar lagoons other science based projects will look at sustainable technical solutions for the remediation of contaminated land, the effect of climate change on pollutant linkages and the use of novel special composts for remediation (WP K). Both the acid tar lagoon (WP H) and the novel compost packages are designated as CL:AIRE research projects.

The restoration of heavily contaminated land in the urban environment requires an inclusive approach and the development of sustainable methods of site remediation which take account of both socio-economic and technical issues.

In this paper we present the initial findings of a multi-disciplinary research programme which is seeking to advance technical and scientific knowledge on remediation of acid tar lagoons. This research is also seeking to develop a technically sound remediation plan for a specific case study site acceptable to all stakeholders.

BACKGROUND

Origin of acid tar

Acid tar is a waste residue of petrochemical processes, which are now mostly abandoned. Its production can be traced from the end of the 19th century (Milne, 1986).

There are three main processes that produce acid tars: benzole refining, white oil production and oil re-refining (Nancarrow et al., 2001). Each involves the use of concentrated sulphuric acid as a washing liquid to purify an organic material, which results in a residual tar containing a high proportion of sulphuric acid compared with other tars from coal carbonization processes.

Benzole refining is a set of processes which extract purified fractions of benzene, toluene and xylene from crude benzole, a by-product of coal carbonization. Washing with concentrated sulphuric acid removes two major impurities: sulphur-containing compounds and unsaturated hydrocarbons (Claxton, 1961). After the washing is complete, the purified benzole is decanted for further treatment and the bottom acid tar is run off from the base of the washer. Although acid tars contain many similar compounds to coal tars, the acid tar is not coal tar plus acid. They are generated from different stages of the coal carbonization process, Figure 1, (Claxton, 1961).

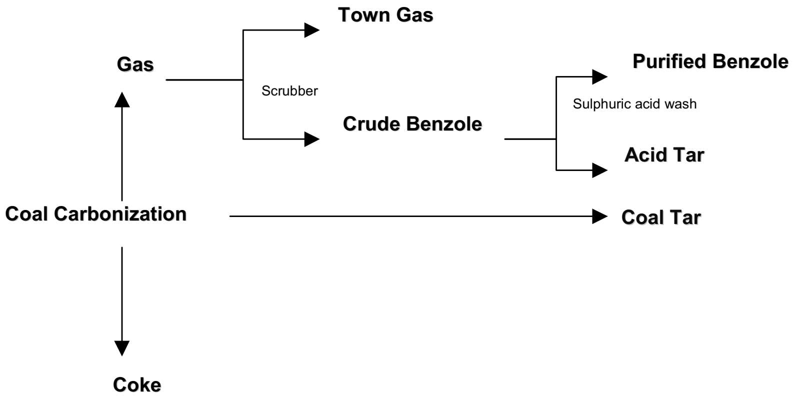

Figure 1, Production of acid tars and coal tars.

Oil re-refining is a process that regenerates spent lubricants. The oil is fed into a contact tank where it is mixed with concentrated sulphuric acid and Fullers earth to remove non-hydrocarbon material, unsaturated hydrocarbons and sulphur-containing compounds (Milne, 1986).

White oils are highly purified compounds used for medicinal, cosmetic and specialized lubrication purposes. Again sulphuric acid is used for removal of unsaturated and sulphur-containing compounds.

Scale of problem

During the period 1930-1980, there were approximately 140 benzole refining plants with an estimated total production of 2.5 million tonnes. White oil production generated an estimated 2 million tonnes of acid tar across ten to twelve sites in the UK. Information about oil re-refining is very limited. There were about 30-40 small plants typically producing 500 tonnes of acid tar per year over an average 40 years operation (Nancarrow et al., 2001).

Acid tar disposal

Historically, the methods used for acid tar disposal were mostly by landfill into existing holes or lined lagoons, usually near the former chemical plants. The tar sometimes underwent a limited pre-treatment, and was often co-disposed with other materials such as drums of various chemicals, sugar waste, sand, ash, clinker, vegetation, PCBs etc. Typical lagoon depths reported in the literature vary from 4-10m, open or capped (1-2m), and volumes vary from ~3000-60000m^3 (Nichol, 2000, Chambers, 2001, Banks et al., 1998).

Before the 1970s, the disposal of acid tar was usually not an environmentally friendly process. In the benzole refining industry, the acid tar produced was often pre-treated by diluting it with creosote oil and then steaming to recover any entrained benzole and some of the sulphuric acid (Claxton, 1961). Some efforts were made to neutralize the acid by mixing the tar with lime and other alkaline materials. However due to poor mixing with the thick tar, this usually proved to be inefficient.

CHARACTERISTICS OF ACID TAR

Composition

The chemical composition of acid tar from each individual process differs significantly due to the different starting material and final product. Therefore the chemical characteristics of acid tar cannot be closely specified. However the basic characteristics of acid tar remain similar across the three major processes. Acid tar is a complex mixture of hydrocarbon, sulphuric acid, water and a various range of co-disposed materials. The chemicals inside acid tar can be grouped into following categories: aliphatic hydrocarbons, aromatic hydrocarbons, phenols, metals, organic acids, sulphonated hydrocarbons and gases such as hydrogen sulphide, sulphur dioxide and methane (Nancarrow et al. 2001). Disturbed tars may thus give rise to significant odour problems. Some tars were pretreated to reduce their acid content before disposal. Nichol (2000) reports a typical composite breakdown of tar as 44% sulphuric acid, 42% oil residues, 8% sulpated oil residues and 6% water.

Physically acid tars consist of three phases: a free tar phase, free oil and a sulphate-rich acidic aqueous phase. The latter will not dissolve in the tar or oil and may exist as an emulsion similar to those found in coal tars (Payne & Charles, 1987) or as pockets of clear liquid (Nichol, 2000).

Physical properties

The viscosity of acid tar is highly sensitive to temperature, at high temperatures the tar will become fairly mobile and tends to be fluid, but at lower temperatures the tar solidifies to a variable degree, depending on its composition. At exposed surfaces, oxidation will occur resulting in an anticipated increase of viscosity within the lagoon surface layers, in some cases leading to surface cracking. The density of the tar is reported at between 1200 and 1400kg/m^3 (Nichol, 2000), which is higher than typical coal tars at 1060 kg/m^3 (Oudijk and Coler, 1995) and it may therefore be regarded as a DNAPL. It is assumed that the higher acid tar density is due in part to the high sulphuric acid content (density 1960 kg/m^3).
Table 1 shows some of physical properties of acid tar from different processes.

Table 1, Physical property of acid tars (Nancarrow et al. 2001).

Origin	Viscosity	pH	Colour	Odour
Benzole refining	Thin to fairly viscous	pH 2 or lower	Generally black	Strongly aromatic
White oil production	Very viscous	The most acidic tars, pH below 1	Generally black	Oily
Oil re-refining	Variable	pH 2 or lower	Browner than others	Oily

Principal contaminants

The major contaminants within acid tar are PAHs, phenols, benzene, toluene, xylene (BTEX), acid, heavy metals and sulphate all of which can cause environmental problems if they migrate into surrounding soil and groundwater environment. Air pollution may be caused by volatile organic compounds (VOCs) and dusts from the weathering of exposed tar surfaces (Nancarrow et al., 2001).

Physical and chemical mobility of acid tar

In any consideration of the environmental impact of an acid tar lagoon, it is necessary to examine both the physical and chemical stability of the tar, each of which are interdependent and must be controlled. Barriers to contaminant migration may be mechanically disrupted while physical barriers may be chemically attacked. Figure 2 depicts a conceptual model of a range of processes and potential migration pathways that have been observed or are inferred for a general acid tar lagoon.

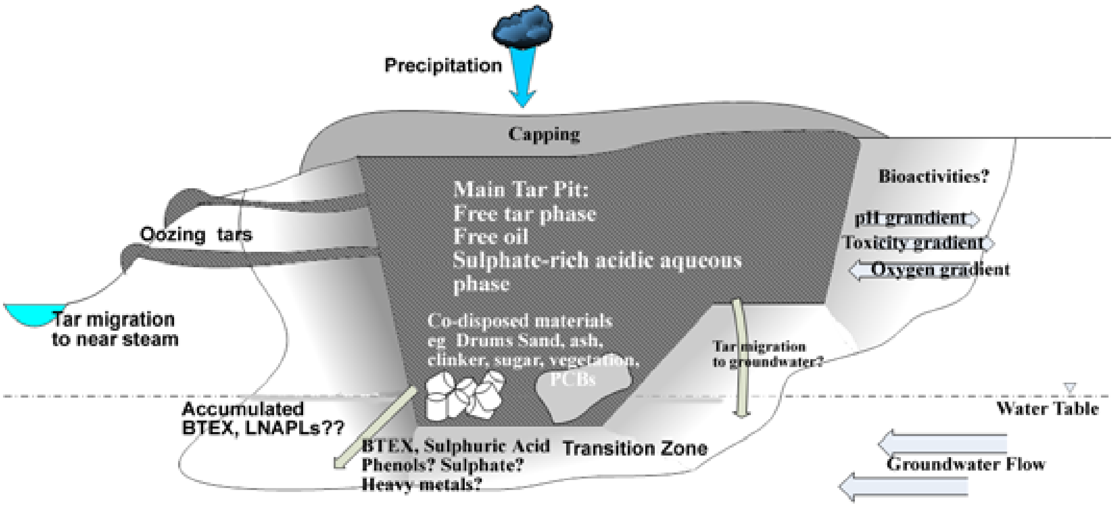

Figure 2, Model of generic acid tar lagoon processes.

Nichol (2000), reports results of probings of an acid tar lagoon that indicate stratification of the tar into semi-solid layers separated by tar bands of softer consistency. Reynolds (2002) reports seismic survey data indicating softer surface tars underlain by more viscous tar. It is not clear whether this is simply due to differing batch properties as tar was placed in the lagoon, or due to long term separation or weathering processes. Semi-fluid tar, driven by the pressure head of the overlying tar and any capping material will find any cracks, and other pathways in the soil e.g. along tree roots etc. The acid will also tend to dissolve components of the mineral matrix helping to widen fissures and ease flow, which it is anticipated, will give rise to unstable fingering (preferential flow paths). Fingering will increase the surface area to volume ratio of the tar and will enhance leaching, oxidation and biodegradation, which in turn will affect the mechanical properties of the flowing tar. If this generates a less viscous DNAPL then further migration may occur, however the original tar is likely to be too viscous to migrate downwards to any great extent except through larger fissures. While biodegradation is unlikely to degrade a significant proportion of contaminants, it may have a significant influence on the physical and chemical mobility of the tar and its constituents.

Acid tar is lighter than soil, and therefore typically heavier capping materials will tend to sink into it. Capping stability will be dependent on a number similar to the Rayleigh number used to characterise the onset of convection in cases of density inversion in stratified fluids.

While it is possible to infer and describe likely processes occurring in and around acid tar lagoons, there exists little scientific data to quantify such processes or to establish their significance.

Environmental impact

Table 2 lists an extensive but not necessarily exhaustive set of potential linkages and environmental impacts of acid tar lagoons. Any restoration will seek to control these linkages to acceptable levels.

Table 2: Acid tar lagoons: potential linkages

Source	Pathway	Receptor
BTEX, PAHs, VOCs	Volatilisation in upper soil surface	Site users
BTEX, PAHs, heavy metals, phenols & sulphate	Inhalation of dust and vapours	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulphate	Ingestion of surface soils	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulphate	Groundwater discharge	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulphate	Surface run off	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulphate	Migration along engineered structures (outfall)	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulphate	Leaching/migration of contaminants through the soil and unsaturated zone	Major/Minor aquifer
Methane, sulphur dioxide and hydrogen sulphide	Migration through permeable soil	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulphate. Acid (burns).	Bulk migration of tar. Direct contact.	Site users, residents of adjacent properties
Toxic combustion products	Smoke from combustion of tar in lagoon	Site users, residents of adjacent properties

CASE STUDIES

This project is based around a specific lagoon, though comparisons will be made with other acid tar lagoons.

The case study site was originally the site of a 7m deep sand pit which was later used for the disposal of domestic waste and included a bunded acid tar lagoon with an estimated volume of 12000m^3. Anecdotal evidence suggests that the lagoon and surrounding site was also used for the disposal of foundry sand and lime. Little detail is available regarding the extent of the acid tar disposal and form of the lagoon as the site was extensively remediated during the 1970's. It would appear that the bund structures were levelled and the site capped with 1 to 3m of soil covering and converted to soft end use. Prior to levelling of the bunds, evidence indicates that an excavation was made close to the lagoon and the excess tar decanted into it by breaching the bund. The site is underlain by sands and gravels above a sandstone aquifer. The site is also bounded by a stream. Recent site investigation data would suggest that both the stream and the aquifer may have been contaminated due to the presence of the acid tar. Additionally, large tar deposits are exposed at the ground surface in areas that have been capped. These areas have been fenced off to stop public access.

THE WAY FORWARD

Technical remediation options need to deal with both physical and chemical stability issues; even if the primary source were removed it is still necessary to address any residual tars and associated plumes. At the same time, the remediation process has to be acceptable to site owners, site users, the wider public, the wider environment and the regulatory authorities; i.e. stakeholders with varying priorities.

It is clear that significant progress is required to characterize more fully mechanical, chemical, and biological processes occurring in and around acid tar lagoons in order to fully realize a robust remediation solution. Issues include chemical compatibility and mechanical stability of containment systems, tar leachability by groundwater, potential for natural attenuation to degrade leachants and changes in tar properties by weathering and time.

Initial work will further characterise the study site, with sampling of the tar at various locations and a geophysical survey. A range of chemical and mechanical laboratory tests on the tar will be undertaken, together with leaching and weathering measurements.

REFERENCES

Banks, D., Nesbit, N.L., Firth, T. & Power, S. 1998. Contaminant migration from disposal of acid tar wastes in fractured Coal Measures strata, South Derbyshire. *In*: Mather, J.D., Banks, D., Dumpleton, S. & Fermor, M. (*eds*.), *Groundwater Contaminants and their Migration*, Geological Society Special Publication 128, 283 - 311.

Chambers, J.E., 2001. The application of 3D electrical tomography to the investigation of brownfield sites, *PHD thesis*, University of Sheffield.

Claxton, G., 1961. Benzoles, production and uses, *The National Benzole and Allied Products Association*, London.

Nancarrow, D.J, Slade, N.J. and Steeds J.E., 2001, Land contamination: Technical Guidance on Special Sites: Acid tar lagoons. *Environment Agency R&D Technical Report P5-042/TR/04*.

Nichol, D., 2000. Geo-engineering problems at Hoole Bank acid tar lagoon, Cheshire, UK. *Land Contamination & Reclamation*, **8**, 167 – 173.

Milne, D.D, Clark, A.I. & Perry, R., 1986. Acid tars: Their production, treatment and disposal in the U.K., *Waste Management & Research*, **4**, 407 – 418.

Oudijk, G. & Coler, M., 1995. Beneficial use of the upwelling phenomenon in coal-tar remediation efforts. *Int. Symp. and Trade Fair on the Clean-up of Manufactured Gas Plants,* September 19-21, 1995, Prague, Czech Republic.

Payne, J.R., Charles, R. ,1987, Petroleum spills in the Marine Environment. The Chemistry and Formation of Water-In-Oil Emulsions and Tar Balls. *Marine Chemistry*, **20**, Issue 3, 297.

Reynolds, J.M, 2002, The role of environmental geophysics in the investigation of an acid tar lagoon, Llwyneinion, North Wales, UK. *First break*, Vol 20, 10 October 2002, 630-636.

Biographical Note

Professor Mike Ramsey

Michael Ramsey, PhD., FRSC. C.Chem. is Professor of Environmental Science and Director of the Centre for Environmental Research at University of Sussex, UK. His BSc in Chemistry and Geology was from Hull University, MSc in Mineral Chemistry from Birmingham University and PhD in Analytical Geochemistry from Imperial College. He worked initially for Roan Consolidated Mines in Zambia including investigations into the environmental impact of mining and processing. He then spent twenty year in the Applied and Environmental Geochemistry Research Group at Imperial College, London. He has published over 90 papers, supervised 13 successful PhD students, and taught field-based environmental sampling to industry/regulators/academics in his annual short course 'Sampling and Analysis of Contaminated Land'. He is currently involved in the preparation a Eurachem guide on the Estimation of Measurement Uncertainty arising from Sampling and is Chair of the Royal Society of Chemistry/AMC Subcommittee on Sampling Uncertainty and Quality.

Cost-Effective Investigation of Contaminated Land: Initial Findings

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Overview

- Context and rationale
- Objectives
- First two case studies
- Initial results
- Conclusions – so far
- Further work

Context and rationale

- How to match expenditure on site investigation to
  - the complexity/heterogeneity/uncertainty of the site
  - the financial consequences of misclassifying the site
- Currently done subjectively by judgement and experience of investigator
  - Not easily justified, or transparent
- Need a decision support tool to
  - Show the optimal approach
  - Can be used to justify better survey – when required

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Objectives (1)

- **Aim**: to develop a prototype decision support tool for Optimized Contaminated Land Investigation (OCLI-TOOL) for use by site investigators
  - to develop cost-effective site investigations on contaminated sites.

Objectives :-

- Assess advantages and limitations of existing OCLI method - by
  - – applying to six contrasting contaminated land sites

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Objectives (2)

- Progressively improve performance and usefulness of OCLI method
  - by incorporating feedback from stakeholders (e.g. site investigators, problem holders, developers, regulators)
  - after each of the six investigations.
- Produce prototype decision support tool version of OCLI method, 'OCLI-TOOL',
  - can be used by site investigators in general, at any site.
- Publicize and explain the benefits of the OCLI method
  - to site investigators & developers of brownfield sites.

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Case Studies – Selection Criteria

- Criteria used to select sites will include the characteristics of:-
- the contamination (type, intensity, extent and heterogeneity),
- the site (size, previous/intended land use and value) and
- the measurements (costs and uncertainty of sampling and analysis).

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Case Studies – Selection Criteria

Criterion	***Sub-division***	***Site 1***	***Site 2***
Contamination	Type	Inorganic (As)	Org (PAH) + Inorg(Pb+As)
	Intensity (conc)	High (c~T)	High (c~T)
	Extent (width/depth)	Large/shallow	Large/shallow
	Heterogeneity	High	High
	Threshold? (T, e.g. SGV)	Yes	Yes
Site	Size	Small/medium	Small
	Value	Low	High
	Consequence Cost**	Low	High
Measurement	Analytical cost	Low	High
	Analytical Uncertainty	Low?	Mod/High?
	Sampling cost	Low/Mod	Mod/High
	Sampling uncertainty	High	High
Logistics	Piggy back on routine SI?	Yes (ideally)	Yes (ideally)
	Routine SI date	Dec 03	Nov03

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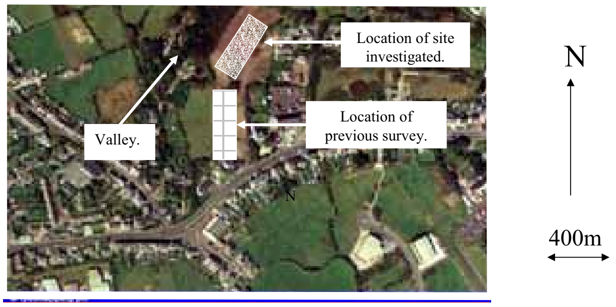
Case Studies

- Site 1: Housing development on old Cornish mine site



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Case Study #1 - Cornwall

16 trial pits were dug across the site (map?)

– sampled by routine investigator – single grab ~650g

Duplicate samples from 8 pits - at 2 depths = 0.5 and 1.5m

- by independent application of the same protocol
- allow for ambiguity & effect of small-scale heterogeneity

Send for analysis to commercial lab

-request 'balanced design' =

-analytical duplicates on sample duplicates

-un-rounded and un-truncated measurements

-problematic in routine lab – not use to it

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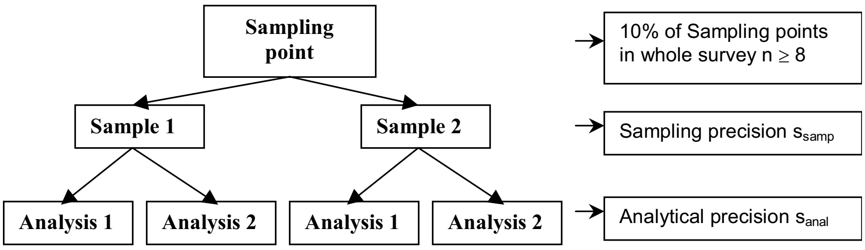
Balanced Sampling Design



→ 10% of Sampling points in whole survey n ≥ 8

→ Sampling precision s_{samp}

→ Analytical precision s_{anal}

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Results from Cornish site

As concentration in soil duplicates mg/kg, at depth 0.5m

- note large variation between samples from the same trial pit

Sample i.d.	S1A1	S1A2	S2A1	S2A2
RR01	153	153	144	144
RR02	412	457	459	477
RR03	314	342	343	419
RR04	124	134	325	315
RR05	125	139	654	723
RR06	675	778	704	676
RR10	837	878	20428	19908
RR14	145	152	257	288

Estimation of Uncertainty

- Robust ANOVA – allows for non-normality
- $U\% = 200s/x_{robust}$ (95% confidence)
- U analysis = 15%
- U sampling = 62%
- U measurement = 64% - dominated by the sampling
- But is there too much uncertainty?
- Only accounts for 21% of the total variance (~FFP < 20%)
- Consider financial consequences – OCLI method

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Cost considerations

- Analysis for Total As = £10 per determination
- Sampling = £30 per sample
- ‘False positive’ *(‘contaminated’ when not)*

  = £6000 per location for unnecessary remediation
    - 10m x 10m plot,
    - cover with 0.4m imported topsoil (£70 /m^3) and
    - geotextile membrane (~£30/m^2)

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Classification of Contamination

- Threshold value:
  - As generic SGV = 20 mg/kg
  - Local As threshold, initial suggestion of 400mg/kg

    Due to locally high background concentration of As
- OCLI optimised for As conc = 500 mg/kg

  - Typical value for false positive mis-classification

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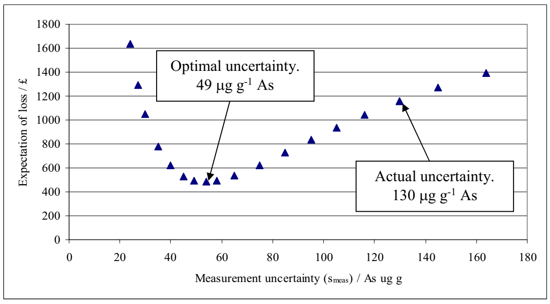
Optimization of Uncertainty



Change of financial loss with increasing uncertainty, *Site 1,Eqn 1*,

- much higher loss ~£1200 at actual uncertainty, than £500 at optimal
- measurements not optimal - improved sampling x3 indicated

-will cost more to reduce U, - less than reduction in expectation of loss

Conclusions (1)

- OCLI method is applicable to routine site investigation
- It is easy to estimate uncertainty (arising mainly from sampling)
  - 64% is not unusual (generally 40-80%)
- Advantages of OCLI
  - -Gives a value of uncertainty *(usually present but unknown)*
  - -Indicates whether this uncertainty will cause problems
  - -Shows how uncertainty can be reduced – if justified financially
  - -Allows you to make reliable decisions, despite the uncertainty/heterogeneity

Conclusions (2)

- Challenges of OCLI – *a few teething problems*

Motivation of contractor

–'duplicate measurement never give same result' – confuse interpretation!

Liaison with lab difficult

- getting design implemented
- unrounded measurements reported
- encourage a good lab to offer a OCLI package?

Extra cost – at small sites there is a higher % cost

Looking into way of reducing this – unbalanced design (-25%)

No analytical duplicates (can't separate sources of U)

Extra training of samplers - does give them feedback on quality of sampling

Further work (1)

Application of OCLI to other sites

Ex-Gasworks site has multiple contaminants

-apply to organic contaminants

-Investigate optimization of system over all contaminants

-Site investigation and chemical analysis complete

-Uncertainty being estimated and OCLI being applied

Further work (2)

Selection of other test sites, several possibilities:-

Lampton Ex- Coking Works – groundwater, monitoring – temporal variation causes uncertainty

Southwark – small high value site – highly heterogeneous – low sampling cost?

Need other sites (Suggestions welcome), with:-

High consequence cost?

Low heterogeneity

Generally low levels of contamination (+ few hot spots)

Depth of contamination – 3D characterisation?

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Acknowledgements

- Dr Paul Taylor – Research Fellow
- Katy Boon – PhD student
- Dr Joe Kelly – Southern Testing
- Rod Smith - John Grimes Partnership
- Mark Williams + Brian Poole - Cornwall Mining Services
- Other Members of Steering Group
- Funding from
  - DTI (ref STBF/004/00034C)
  - CL:AIRE (RP4)

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Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

Cost-Effective Investigation of Contaminated Land: Initial Findings

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ABSTRACT

The first application of the Optimised Contaminated Land Investigation (OCLI) method to a routine site investigation has demonstrated the practicality of the method and the usefulness of its results. In the first case study a high level of uncertainty was determined (64% of the concentration value, at 95% confidence), and the source was identified as the sampling rather than the analytical procedure. Calculations suggest that taking 9-fold composite samples, rather than single grab samples, for each trial pit will reduce the uncertainty by a factor of three, This will reduce the expectation of loss by a factor of three from £1200 to £500 per sampling location, making it a much more cost-effective and reliable site investigation.

INTRODUCTION

Deciding upon the optimal level of expenditure for a site investigation currently depends upon the subjective judgement of an investigator, often based upon years of experience. It requires a balance to be made between many conflicting factors. One important factor is the expected complexity of the contamination at the site. This is often evident in a high level of small-scale heterogeneity of the contaminant concentration, which causes a large degree of uncertainty in estimates of the extent and intensity of the contamination across the site. A second equally important factor is the financial considerations, such as the cost of the investigation and also the potential costs that may arise as a consequence of misclassifying the contamination at the site. The balancing of such factors by an expert can be effective, but it is not always clear how the conclusion has been reached. This may make it difficult to justify a high-cost investigation, when the expert considers it justified. A new approach to finding this balance is to use a mathematically-based decision support tool to identify the optimal approach. This can be used by less experienced investigators, and also allows experts to justify a better survey in a transparent way, when it is required.

The overall aim of this research project is therefore, to develop a prototype decision support tool for Optimized Contaminated Land Investigation (OCLI-TOOL) for use by site investigators to develop cost effective investigations on contaminated sites.

The individual objectives of the project are:-

1. To assess the advantages and limitations of the existing OCLI method, by applying it to a series of six contrasting contaminated land sites
2. To progressively improve the performance and usefulness of the OCLI method by incorporating feedback from stakeholders (e.g. site investigators, problem holders, developers, regulators) after each of the six investigations.
3. To produce a prototype decision support tool version of the OCLI method, called OCLI-TOOL, that can be used by site investigators in general, at any site.
4. To publicize and explain the benefits of the OCLI method to the site investigation community, and to developers of brownfield sites.

This paper aims to describe the progress that has been made in the first six months of the two year project. It will explain the criteria upon which the initial test sites have been selected, and the practicalities of applying the OCLI method to routine site investigations being undertaken for other purposes. It will discuss the advantages and limitations of the OCLI method that have been identified so far, and suggest how improvements can be made in subsequent applications.

CRITERIA FOR SELECTION OF TEST SITES

In order to test out the OCLI method under a wide range of realistic conditions, the sites have been selected to have contrasting expected properties (Table 1).

Table 1. Site selection criteria for OCLI method, and qualitative values for the first two sites. * Site Investigation (SI) are 'piggy backed' onto a routine site investigation. **Consequence Cost is the cost of making error, e.g. unnecessary remediation, leaving undetected contamination in place

Criterion	***Sub-division***	***Site 1***	***Site 2***
Contamination	Type	Heavy Metal (As)	Org (PAH, TPH) + Pb+As
	Intensity (concentration)	High (c~T)	High (c~T)
	Extent (width/depth)	Large/shallow (<0.5m)	Large/shallow (<0.5m)
	Heterogeneity	High	High
	Threshold? (T, e.g. SGV)	Yes	Yes
Site	Size	Small/medium	Small
	Value	Low?	High
	Consequence Cost**	Low	High
Measurement	Analytical cost	Low	High
	Analytical Uncertainty	Low?	Med- High?
	Sampling cost	Low/Mod	Mod/High
	Sampling uncertainty	High	High
Logistics	Piggy back* on routine SI?	Yes	Yes
	Routine SI date	Dec03	Nov03

The first two sites have different types of contamination, ranging from heavy metals alone at Site 1, to a range of organic and inorganic contaminants at Site 2. This difference has a direct bearing on the analytical cost. One key requirement was that a routine site investigation was scheduled to take place on the site, upon which the test of the OCLI method could be 'piggy backed'.

CASE STUDIES

Site 1: Cornish housing development on an ex-mine site

This 400m x 200m site was know to be contaminated with As and to a lesser extent with other heavy metals, due to Sn/Cu mining at the site in the 18th and 19th century

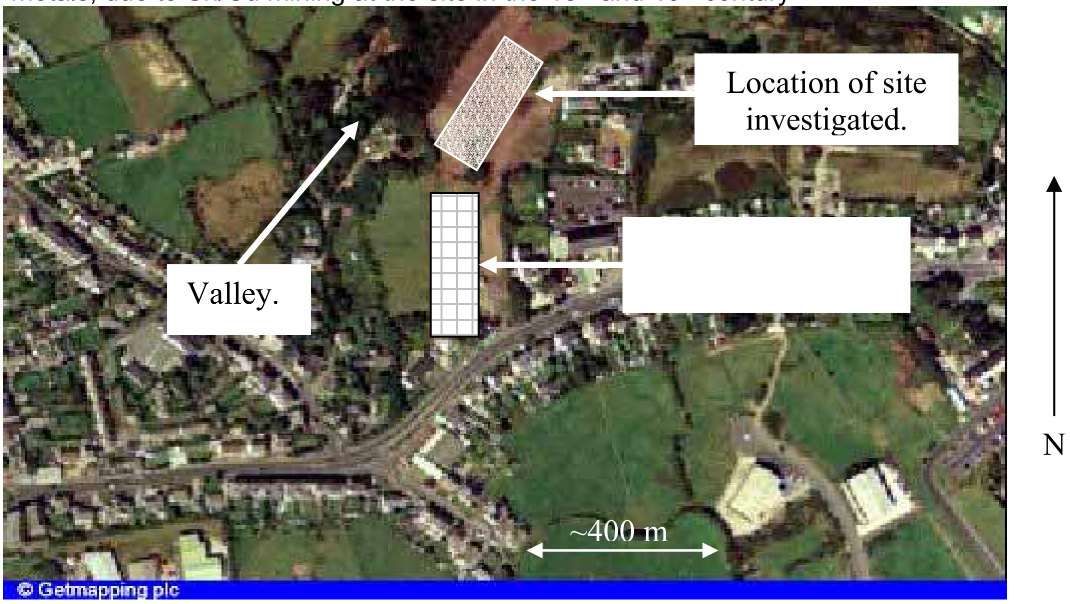


Fig 1. Location of Site 1 in Cornwall

Sixteen trial pits were dug across the site by a primary investigator (i.e. site contractor) as part of a routine site investigation The contactor's objective was to assess the extent of contamination and to select the most appropriate method and extent of remediation that would be required to enable the building of domestic housing. In order to apply the OCLI method to the investigation, the simplest of four possible methods of estimating the uncertainty in the measurements of contamination was selected (Ramsey and Argyraki, 1997). This involved the taking of duplicate samples (650 g, single grab samples) from 8 of the trial pits. These duplicates were taken by the contactor, under the direction of a project member, using an independent re-application of the same sampling protocol to each of these pits. The duplicate samples where therefore not identical, but taken in a way that reflected both the small-scale heterogeneity of the contaminant in the sampling location, and the ambiguity that can arise in the interpretation of the sampling protocol. The procedure was repeated for two different depths of investigation at 0.5 and 1.5m below ground surface.

The duplicate samples were both analysed twice for As, in a balanced design (Fig 2) to enable the source of the uncertainty to be identified.

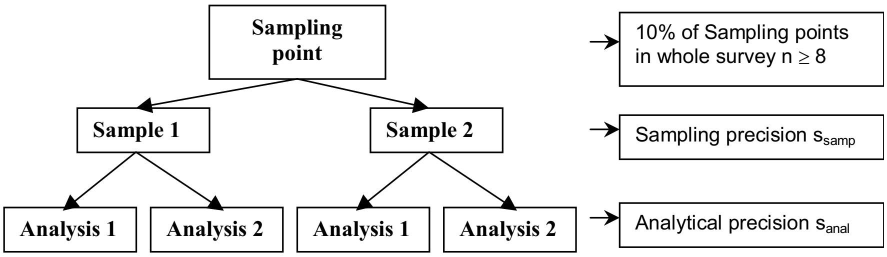


Fig.2. Balanced design of sampling for the estimation of uncertainty

Chemical analysis was performed by a routine analytical laboratory selected by the primary investigator. The lab was asked to implement the balanced design and to supply all of the measurements on the samples, together with the analytical quality control (AQC) information, in an un-rounded, un-truncated format (e.g. actual measurements, rather than some values just as '<detection limit').

RESULTS

For the Cornish site, the analytical duplicates for As agree well (Table 2, rows 1&2 and 3&4), but some of the sample duplicates disagree by a large factor (e.g. more than x10 for location RR10).

Table 2. Comparison of As concentration in 8 trial pits as estimated by a single grab sample (in bold) and that from the full balanced design (Fig 2) at depth of 0.5m. Although the analytical duplication is quite good, the sample duplicates show some large differences caused by small-scale heterogeneity (e.g. location RR10)

	Total As in soil / $\mu g\ g^{-1}$			
	Sample 1		Sample 2	
Sample location	**Analysis 1**	Analysis 2	Analysis 1	Analysis 2
RR01	**153**	153	144	144
RR02	**412**	457	459	477
RR03	**314**	342	343	419
RR04	**124**	134	325	315
RR05	**125**	139	654	723
RR06	**675**	778	704	676
RR10	**837**	878	20428	19908
RR14	**145**	152	257	288

This reflects the high degree of heterogeneity of As within some trial pits. This conclusion was confirmed quantitatively by the use of robust ANOVA (analysis of variance). The total measurement uncertainty was 64%, when expressed as a proportion of the concentration at 95% confidence. It also showed that the analytical uncertainty was small (16% relative), but the sampling uncertainty was large (62% relative), and dominated the total uncertainty, contributing 94% of the total variance.

An important question is whether this high level of uncertainty prevented the measurements being fit-for-purpose (FFP), and giving a reliable interpretation of the contamination. According to one criterion, the measurements are just on the limit of being FFP, as the measurement variance contributes approximately 20% to the total variance (Ramsey *et al.*, 1992).

The OCLI method, described in full elsewhere (Ramsey *et al.,* 2002), considers not just the variance, but also the financial consequences of misclassifying the land in its FFP criterion. The scenario considered here is for a 'false positive' classification in which the soil has a measured As concentration that exceeds the threshold value (T) and therefore requires remedial action, but the true value of concentration is below T and would not require this expenditure. The appropriate value of T for this site is the site-specific SGV for As, suggested used by the local authority in this case as being probably 400 mg/kg. This is higher than the generic SGV for As of 20 mg/kg because of the high background concentration of As in this area of Cornwall.

The cost of remediation, which in this scenario is not always justified, is estimated as £6000 per sampling location. This is based upon the preferred method of covering each plot (10m x 10m) where measured contaminant concentration (c) exceed the threshold (T) with a geotextile membrane (cost £30 m^{-2}) and of depth of 0.4m of clean top soil (cost £70 m^{-3}). The investigation costs include that for taking each field sample (£30) and that for each chemical analysis (£10). The OCLI method uses Equation 1 to calculate the expectation of financial loss E(L).

$$E(L) = C\,[1 - \Phi(\varepsilon_1 / s_{meas})] + D/s^2_{meas} \qquad \ldots\ldots\ldots..(1)$$

The first term of this equation gives the probable financial loss from a misclassification of contaminant concentration at a sampling point by multiplying the total consequence cost (C) by the probability of the misclassification being indicated (e.g. as c>T). The error limit (ε_1) in this case is set as

$$\varepsilon_1 = |T - c|$$

The financial loss can only arise therefore, when the error is large enough to cause a misclassification and therefore a decision error. The standard normal cumulative distribution function (Φ) is used to derive the probability that s_{meas} will exceed ε_1, and hence that the true contaminant value will either exceed T (e.g. a 'false negative' classification) or not exceed T (e.g. a 'false positive' classification). The second term in the equation expresses the cost of making the measurements, where D is the overall measurement cost per unit variance. The loss function can be calculates for a range of values of uncertainty (Fig 3) and usually has a minimum value of cost at some particular optimum value of uncertainty denoted by s'_{meas}.

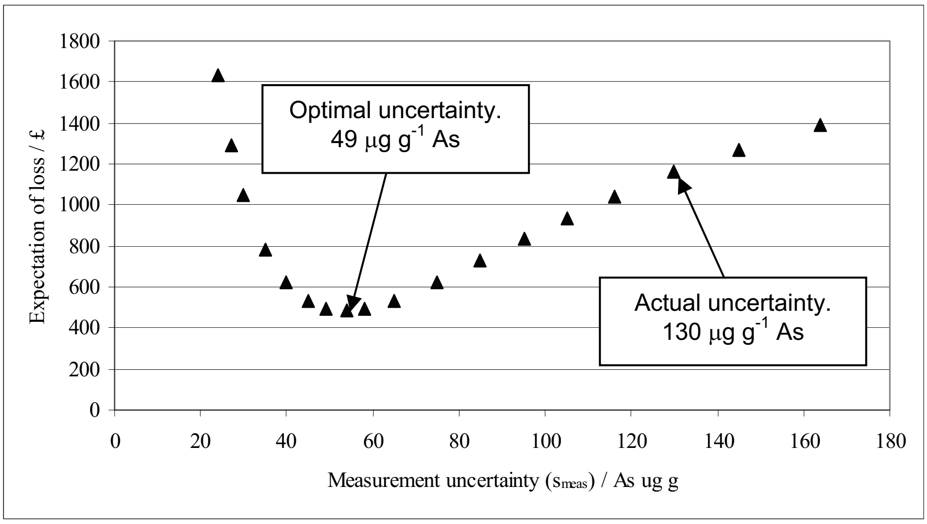


Fig 3. Change of financial loss with increasing uncertainty for Site 1, from Equation 1, showing much higher loss of around £1200 at the actual uncertainty, than the £500 at the optimal value

The actual value of uncertainty of the measurements that were made (130 µg g^{-1}) generate an expectation of loss of £1200 per location. This is well above the £500 expectation of loss at the optimal value of uncertainty (49 µg g^{-1}). A reduction in the uncertainty is indicated therefore. This can best be achieved by a 3-fold reduction in the uncertainty. The OCLI method can also be used to calculate that this improvement can be achieved most cost-effectively by reducing the sampling uncertainty from 130 to 49 µg g^{-1} . Sampling theory can be employed to calculate that this can best be achieved by taking a nine-fold composite sample in each trial pit, instead of the single grab sample. This would however cost an estimated extra £200 per location. This increased initial expenditure is fully justified by the £700 reduced expectation of loss overall.

CONCLUSIONS AND FURTHER WORK

This first application of the OCLI method to a routine site investigation has proved that the method is both feasible and useful. It showed in this initial application that the level of uncertainty was high (64% relative, at 95% confidence) and that the main source (94%) of uncertainty arose from the primary sampling, not from the chemical analysis. One of the substantial advantages of the OCLI approach is that it provides, for the first time, a quantitative estimate of the uncertainty in the measurement of the contaminant concentration. This is necessary for the later steps of OCLI, but it is useful in its own right as a measure of reliability. The OCLI method shows that this level of uncertainty (64%) is substantially higher that the optimal value (24%), and also that the main cause of this uncertainty is the inability of this sampling protocol to overcome the effect of the small-scale heterogeneity within the sampling locations (i.e. trial pits). OCLI also indicates that the uncertainty is likely to cause unnecessary higher financial losses, due to some unnecessary remediation. It indicates that this uncertainty and financial loss can be reduced by improving the sampling protocol to include the taking of 9-fold composite samples. Whether this improved protocol is applied in a supplementary investigation of this site, or is applied to a subsequent investigation at similar sites, will require further consideration.

One current practical challenge in applying the OCLI method to routine site investigations is that it is difficult to motivate the typical site investigator. They have expressed a suspicion that duplicate samples ‘never give the same measurements’ and therefore make interpretation ‘more difficult’ and less certain. The current ‘deterministic approach’ in which a simple action is required if a single concentration measurement (c) is greater than the threshold (T) is undemanding, but as shown here, prone to decision errors and increased expectation of financial loss. The OCLI method enables a ‘probabilistic approach’ that recognises that uncertainty exists and allows for it in a more reliable method of interpretation.

A second related practical challenge is justifying the extra initial cost required to implement the OCLI method. For small site, this is a higher proportion of the cost of the investigation (75%? in this case). One possible solution is to develop an alternative experimental design (e.g. un-balanced) that would reduce the cost of estimating uncertainty. A second solution is the dissemination of case studies in which the substantial overall financial savings enabled by the OCLI method are made explicit. A third possible solution is to include estimation of uncertainty from sampling as a statutory requirement of site investigation reports, in which case there would be little extra cost required to implement OCLI.

The third practical challenge is in the liaison with the analytical laboratory. The existing systems of submitting samples to laboratories are not well suited to extracting all of the information required for implementing OCLI (e.g. using balanced design, reporting un-truncated measurements). Such information usually exists, but most labs are not used to organizing and report it in the form required. It might be advantageous to recruit one lab to produce an ‘OCLI package’ that investigators can purchase, which includes all of the require features.

The next step is to apply OCLI to more of the sites with contrasting properties, to find out how generally applicable these initial observations are, and to test the method further. Site 2 has already been sampled and the interpretation will look at the application of OCLI to a site with organic contaminants, and also how the approach can be adapted to the situation of multiple simultaneous contaminants. Two further site investigations are being organized in which the effects of lower sampling costs and of higher site value will be investigated, and also the sampling of groundwater rather than soil, considered in order to assess potential risk.

ACKNOWLEDGEMENTS

This work has been funded from DTI contract STBF/004/00034C and CL:AIRE research project RP4. The help of Rod Smith at John Grimes Partnership and Mark Williams and Brian Poole at Cornwall Mining Services is gratefully acknowledged

REFERENCES

Ramsey, M. and A. Argyraki. 1997. “Estimation of measurement uncertainty from field sampling: the implications for the classification of contaminated land.” *The science of the total environment* **198**: 243-257.

Ramsey, M., M. Thompson and M. Hale (1992). “Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance.” *Journal of Geochemical Exploration* **44**: 23-26.

Ramsey M.H., Taylor P. D. and Lee J.C. (2002) Optimized contaminated land investigation at minimum overall cost to achieve fitness-for-purpose, *Journal of Environmental Monitoring*, **4**, 5, 809 – 814

DEFRA/ EA (2002) CLEA 2002 Department for Environment, Food and Rural Affairs (DEFRA) and the Environment Agency (EA), SGV 1 Soil Guideline Values for Arsenic Contamination

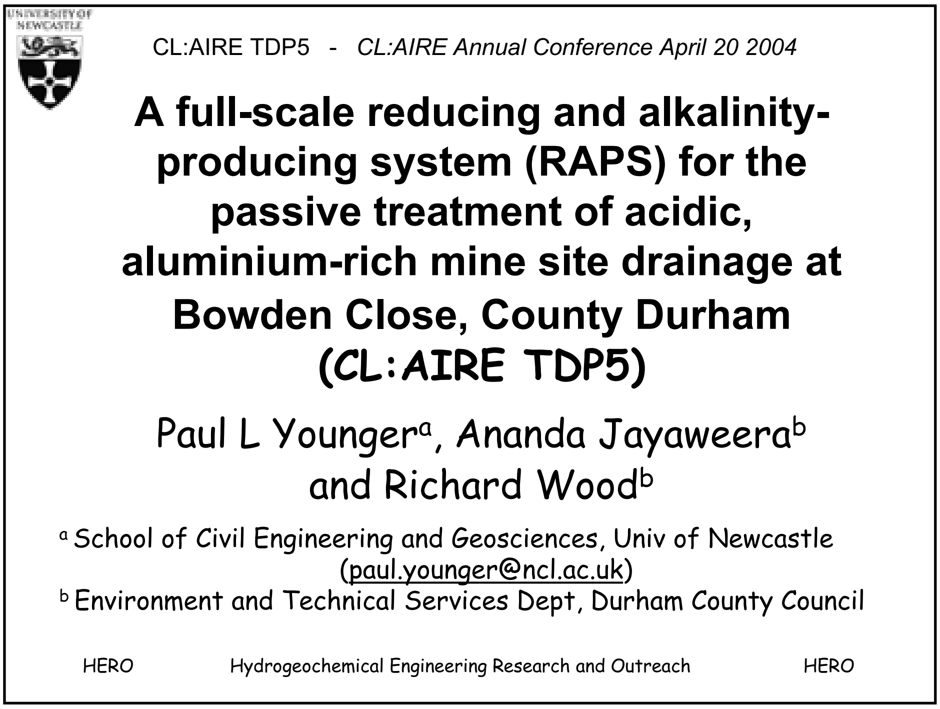
Biographical Note

Professor Paul Younger

Paul L Younger is Professor of Hydrogeochemical Engineering at the University of Newcastle, based in the 5-rated School of Civil Engineering and Geosciences. Paul holds BSc (First Class Hons, Geology) and PhD (Civil Engineering) degrees from Newcastle and an M.S. (Hydrogeology) from Oklahoma State University, where he was a Harkness Fellow from 1984-86. Paul is a Chartered Geologist and a Chartered Engineer who specialises in mine water management, particularly in the remediation of pollution from abandoned mine sites. In this regard, Paul leads Europe's largest and most successful mine water research team, with substantial funding from EPSRC, NERC, the Coal Authority, the Environment Agency, the Mineral Industry Research Organisation and private consulting and mining companies. Paul coordinated the two main European Union Fifth Framework R&D projects dealing with mine waters: PIRAMID (www.piramid.org) and ERMITE (www.minewater.net/ermite). He is now Coordinator of CoSTaR, CL:AIRE's national facility for mine site remediation research, which has recently been designated an 'International Access Research Infrastructure' by the EU, who will fund use of the facility by researchers from all round Europe for the next four years. A fluent Spanish speaker, Paul also has an extensive portfolio of professional experience in Spain and Latin America, as well in the USA and South Africa. He has published more than 150 papers in the international literature, and is lead author of the compendious new volume 'Mine Water: Hydrology, Pollution, Remediation' (Kluwer, Feb 2002). Paul has served on the Freshwater Sciences Peer Review Committee of NERC, and on the Editorial Boards of two international journals (Quarterly Journal of Engineering Geology and Hydrogeology (Geol Soc of London), and Mine Water and the Environment (Springer)). In addition to his academic duties, Paul also holds Directorships in two firms (NuWater Ltd and Project Dewatering Ltd).

A full-scale reducing and alkalinity-producing system (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham

Paul Younger



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A full-scale reducing and alkalinity-producing system (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham
(CL:AIRE TDP5)

Paul L Younger[a], Ananda Jayaweera[b] and Richard Wood[b]

[a] School of Civil Engineering and Geosciences, Univ of Newcastle (paul.younger@ncl.ac.uk)
[b] Environment and Technical Services Dept, Durham County Council

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"The past we inherit, the future we build"

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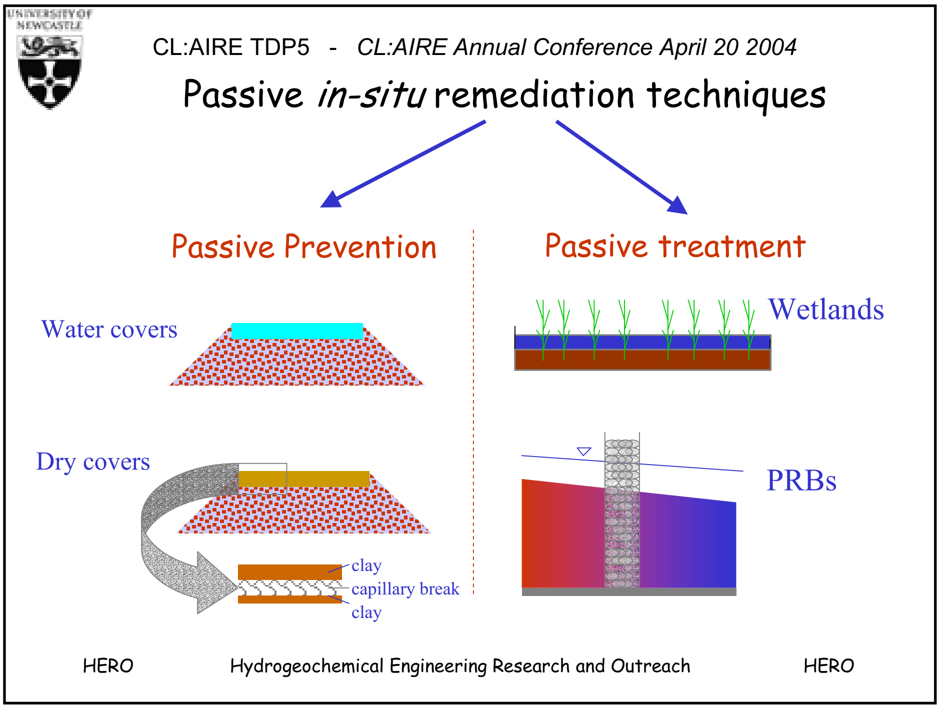

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Passive *in-situ* remediation techniques

Passive Prevention

Water covers

Dry covers

clay
capillary break
clay

Passive treatment

Wetlands

PRBs

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Al-rich leachates

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Al-rich leachates - some UK examples

Site	Al concentration (mg/l)
Quaking Houses, Co Durham	21
Randolph Bing, Fife, Scotland	800
Baads Bing, West Lothian, Scotland	80
Shilbottle Brass Heap, Northumberland	298
Nailstone Colliery Spoil, Leicestershire	73
Bowden Close Colliery, Co Durham	50
Upleatham Ironstone Mine, Cleveland	164

N.B. The proud owner in most cases is now the local authority

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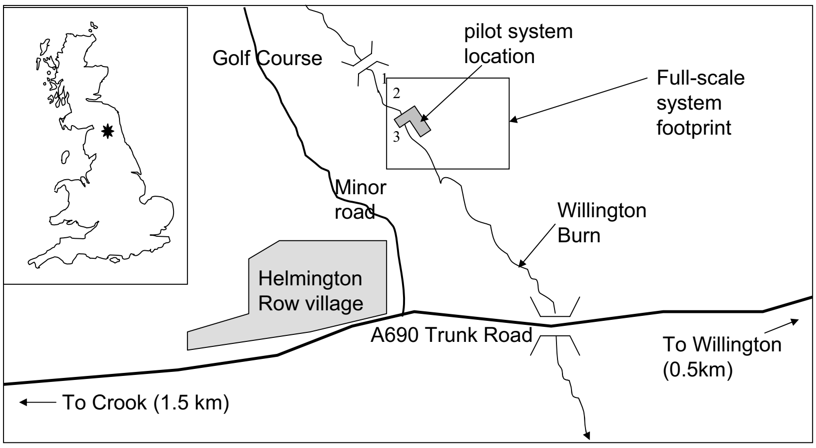
Bowden Close - where?



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A full-scale reducing and alkalinity-producing system (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham

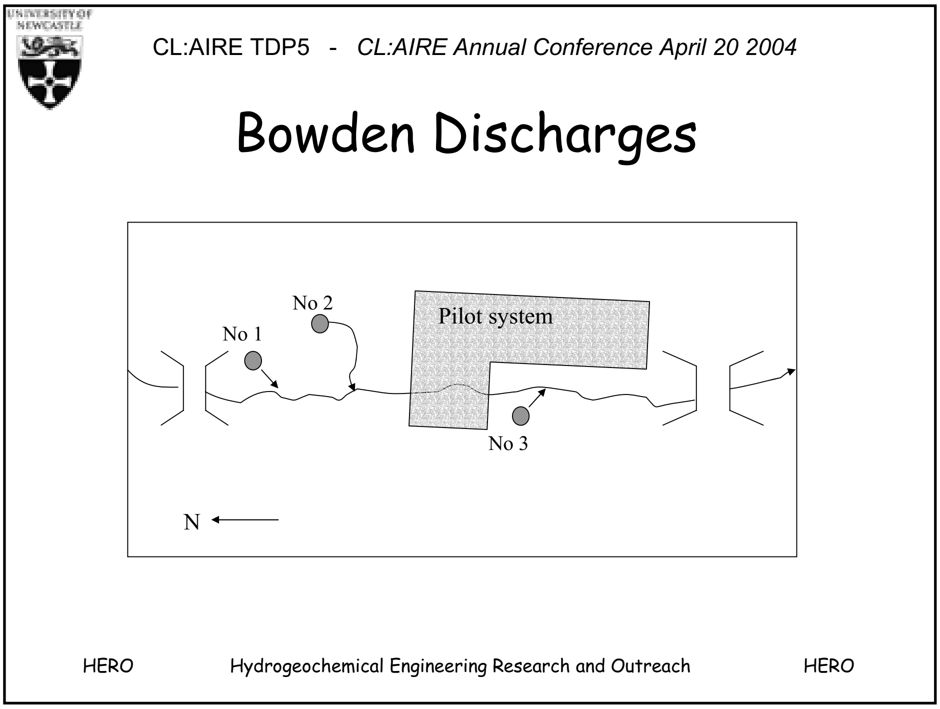
Paul Younger

Bowden Close Pilot System

- Acid waters draining into Willington Burn from otherwise-reclaimed Bowden Close Colliery Site since 1960s - severe impact
- Pilot RAPS / wetland constructed 1999 (funded by CDENT / Durham Co. Council)
- Monitored by N'cle Univ mine water team for 18 months (until FMD outbreak)
- Encouraging results favoured planning for full-scale system

Bowden Close - what?

(Discharges and Impacts)



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Bowden Discharges

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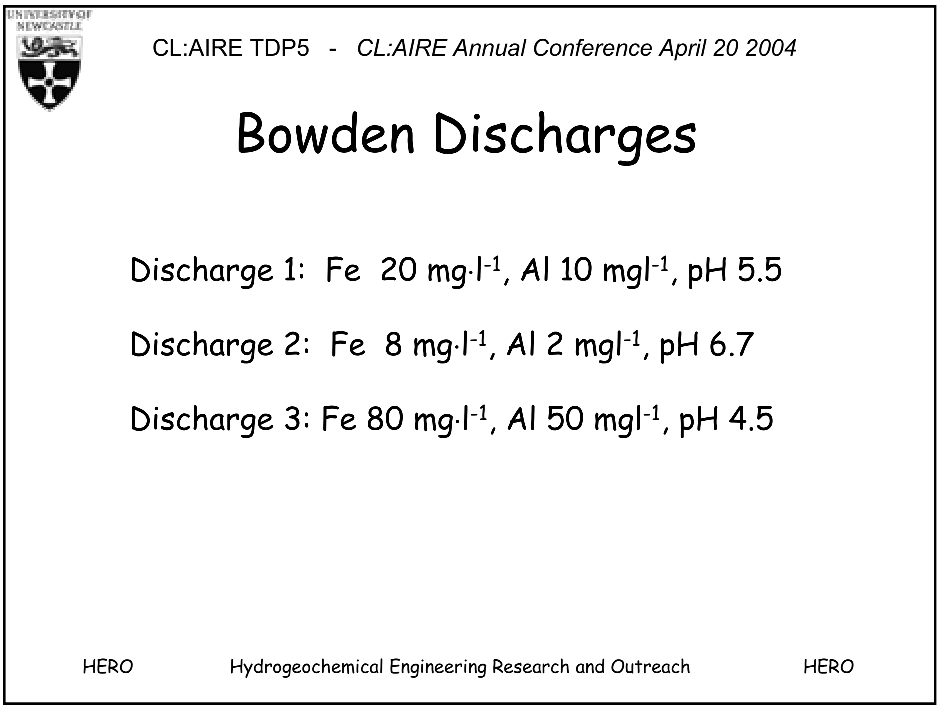

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Bowden Discharges

Discharge 1: Fe 20 $mg{\cdot}l^{-1}$, Al 10 mgl^{-1}, pH 5.5

Discharge 2: Fe 8 $mg{\cdot}l^{-1}$, Al 2 mgl^{-1}, pH 6.7

Discharge 3: Fe 80 $mg{\cdot}l^{-1}$, Al 50 mgl^{-1}, pH 4.5

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Bowden Discharges

Treated in pilot system:

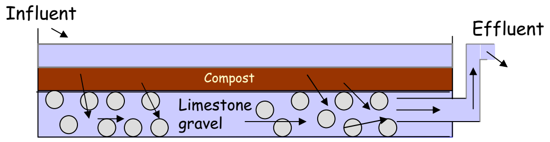
Discharge 1: Fe 20 mg·l^{-1}, Al 10 mgl^{-1}, pH 5.5

Discharge 2: Fe 8 mg·l^{-1}, Al 2 mgl^{-1}, pH 6.7

Discharge 3: Fe 80 mg·l^{-1}, Al 50 mgl^{-1}, pH 4.5

RAPS technology ...

Reducing & Alkalinity Producing Systems (RAPS) for acidic mine waters where there is sufficient head



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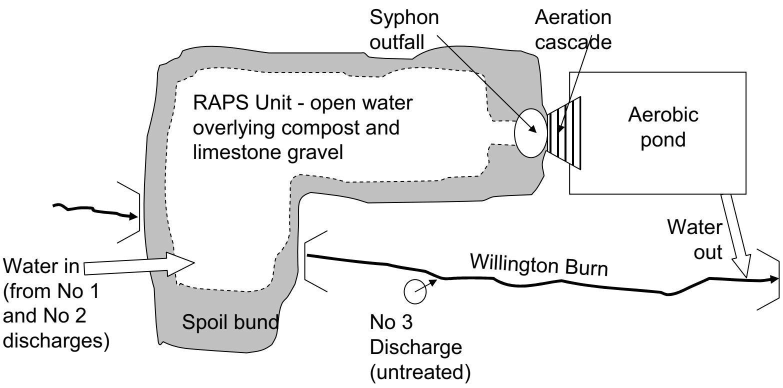
Pilot system layout



Syphon outfall

Aeration cascade

RAPS Unit - open water overlying compost and limestone gravel

Aerobic pond

Water out

Willington Burn

Water in (from No 1 and No 2 discharges)

Spoil bund

No 3 Discharge (untreated)

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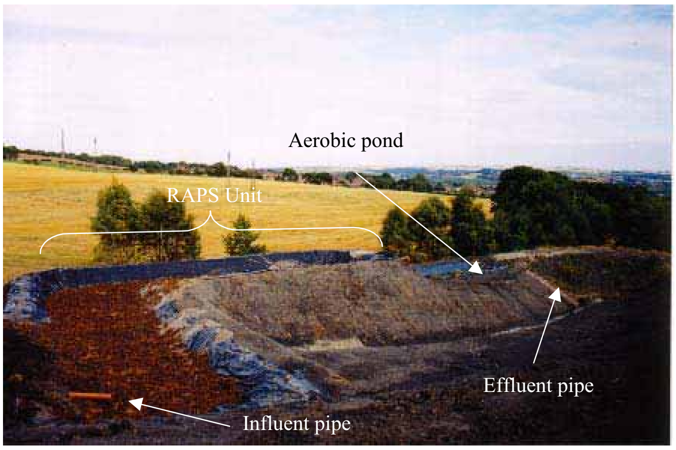
Pilot system



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Pilot system at first commissioning

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Pilot system - aerobic pond downstream of RAPS

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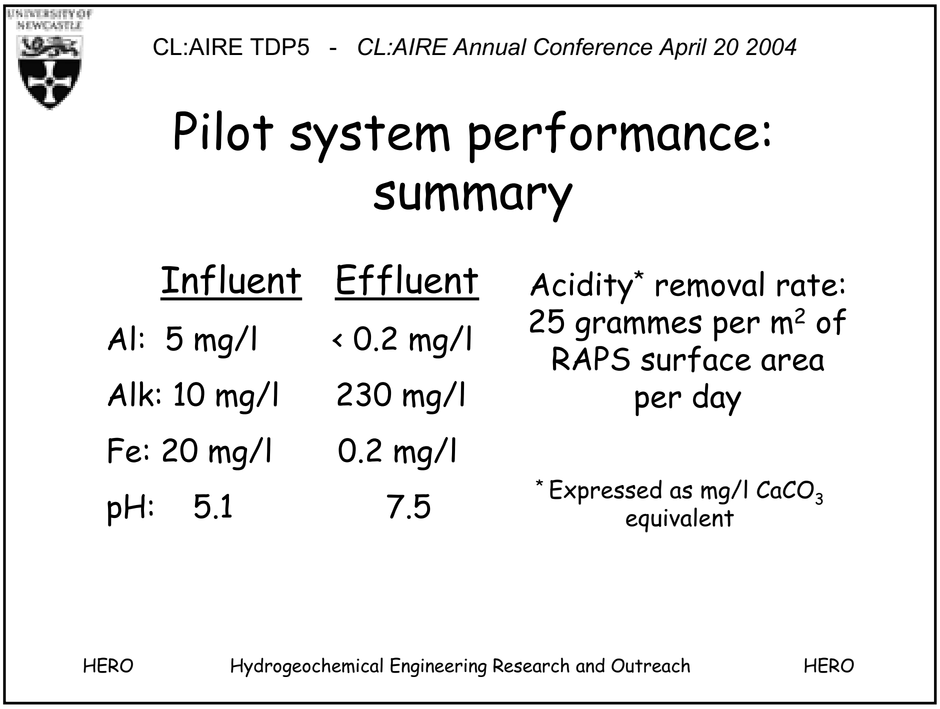

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Pilot system performance: summary

	Influent	Effluent
Al:	5 mg/l	< 0.2 mg/l
Alk:	10 mg/l	230 mg/l
Fe:	20 mg/l	0.2 mg/l
pH:	5.1	7.5

Acidity* removal rate: 25 grammes per m^2 of RAPS surface area per day

* Expressed as mg/l $CaCO_3$ equivalent

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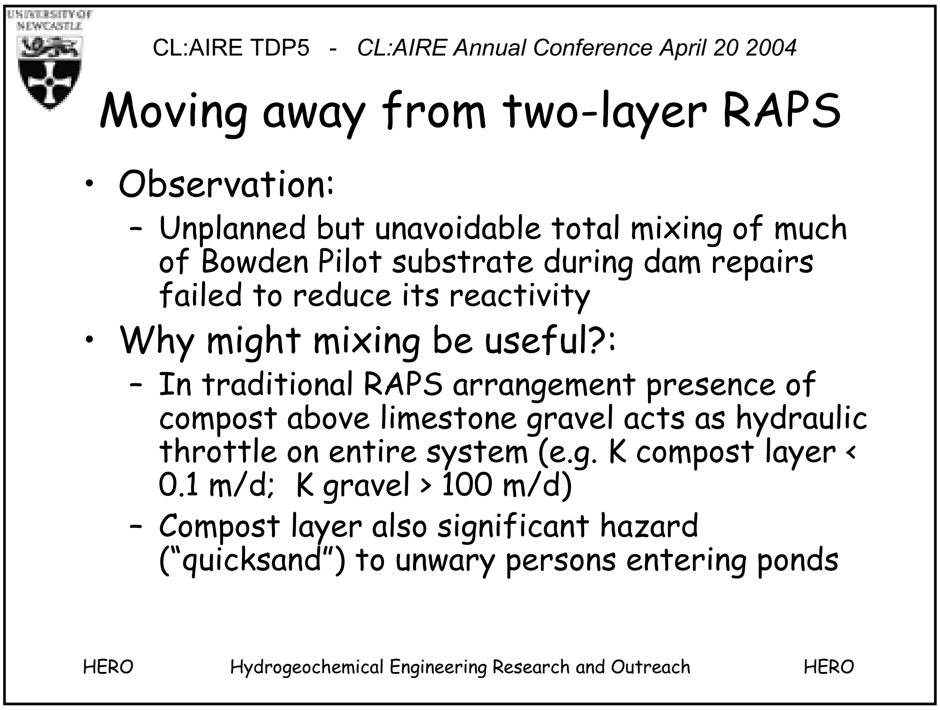

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Moving away from two-layer RAPS

- Observation:
  - Unplanned but unavoidable total mixing of much of Bowden Pilot substrate during dam repairs failed to reduce its reactivity
- Why might mixing be useful?:
  - In traditional RAPS arrangement presence of compost above limestone gravel acts as hydraulic throttle on entire system (e.g. K compost layer < 0.1 m/d; K gravel > 100 m/d)
  - Compost layer also significant hazard ("quicksand") to unwary persons entering ponds

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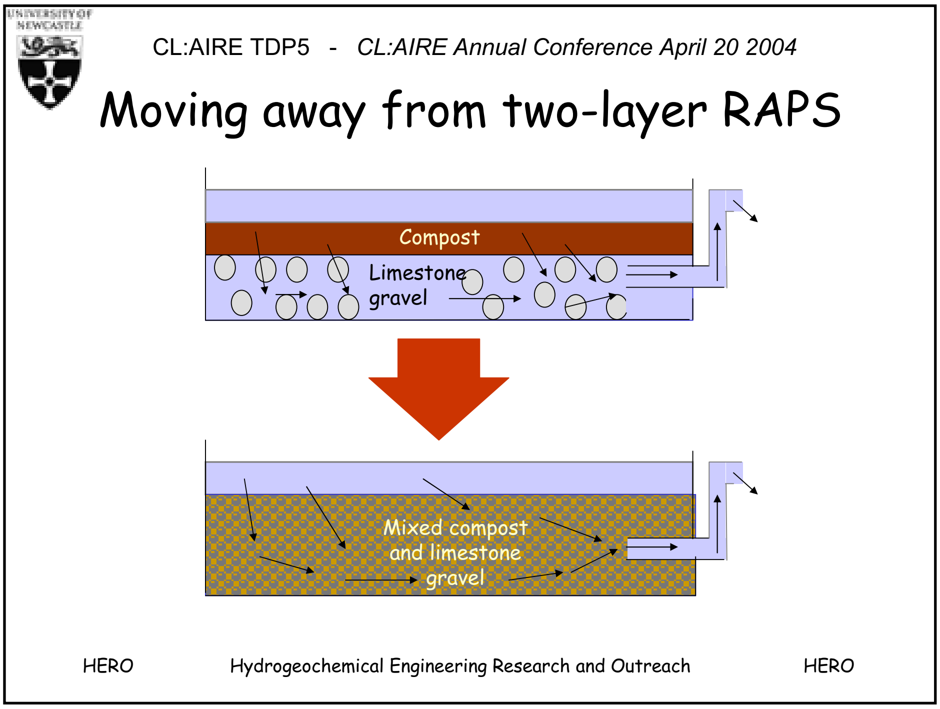

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Moving away from two-layer RAPS

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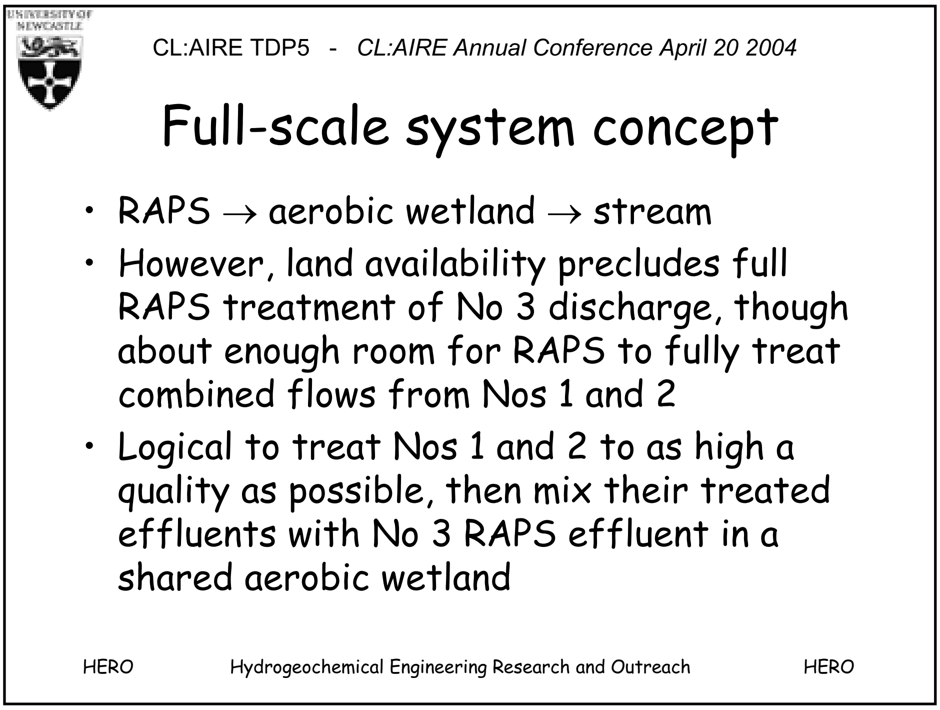

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Full-scale system concept

- RAPS → aerobic wetland → stream
- However, land availability precludes full RAPS treatment of No 3 discharge, though about enough room for RAPS to fully treat combined flows from Nos 1 and 2
- Logical to treat Nos 1 and 2 to as high a quality as possible, then mix their treated effluents with No 3 RAPS effluent in a shared aerobic wetland

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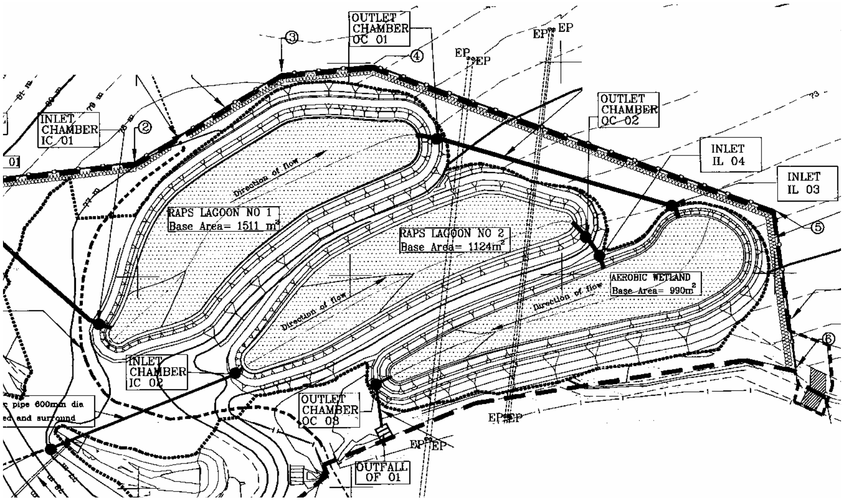
Layout – full-scale system



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Ideal versus actual areas of component passive treatment units in the Bowden Close passive treatment system

Element of system	Ideal area[a] (m^2)	Actual area (m^2)
RAPS 1	**1728**	**1511**
RAPS 2	**4350**	**1124**
Aerobic wetland	**1300[b]**	**990**

[a] as suggested by loading-based design calculations

[b] Assumes a flow-weighted average of 15 mg/l Fe coming from RAPS 1 and RAPS 2.

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Bowden Close full-scale: construction

23.10.2003

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Just after completion of main construction phase

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Just after completion of main construction phase

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Discoveries during construction

- True identity of discharge No 1 revealed …

  … holing into old mine access drift from surface into Harvey Seam
- Implications:
  - management of mine gas hazards
  - subsidence concerns

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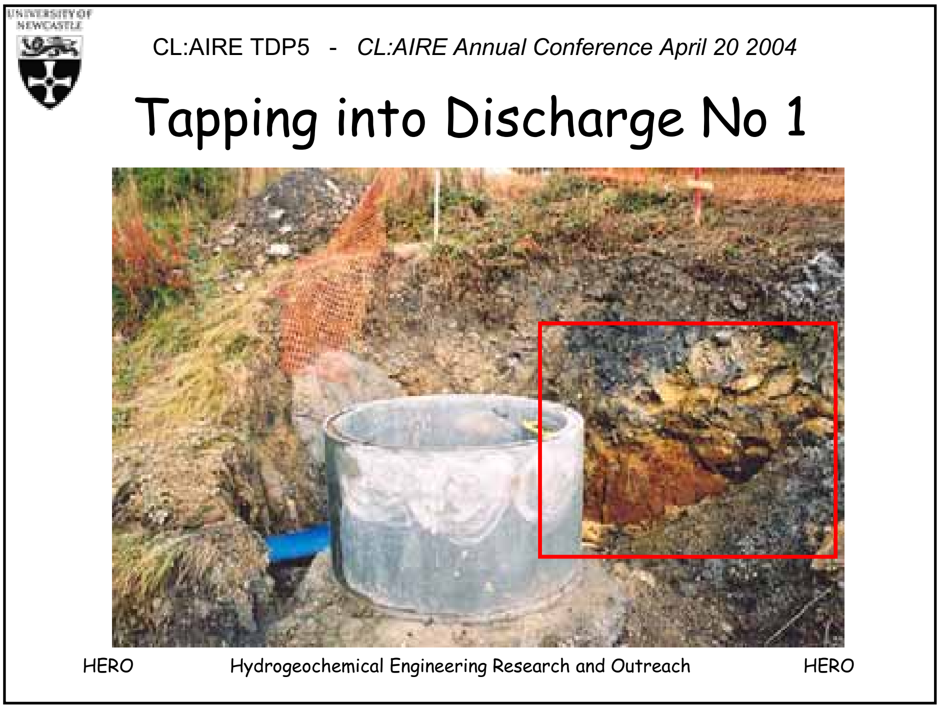

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Tapping into Discharge No 1

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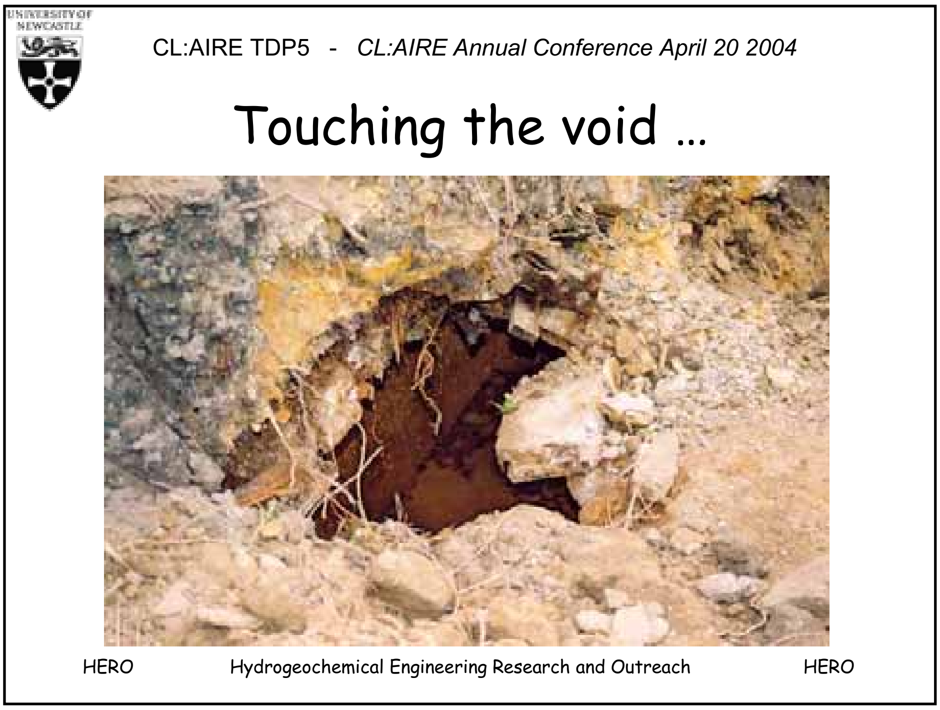

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Touching the void …

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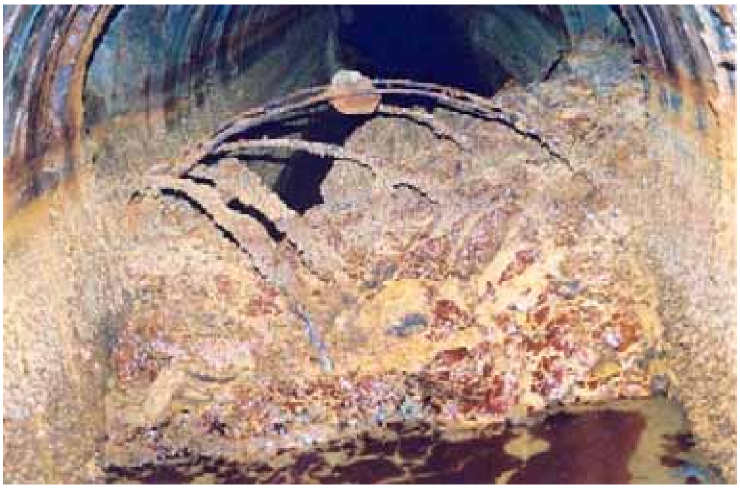
What lies beneath …



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Better out than in …

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Not going quietly …

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Novelties in full-scale system design

- 'Scour pipe' underdrain for periodic flushing out of $Al(OH)_3$ flocs
- Unparalleled secure facilities for continuous monitoring of flow, water quality and piezometry funded by CL:AIRE / BOC Foundation

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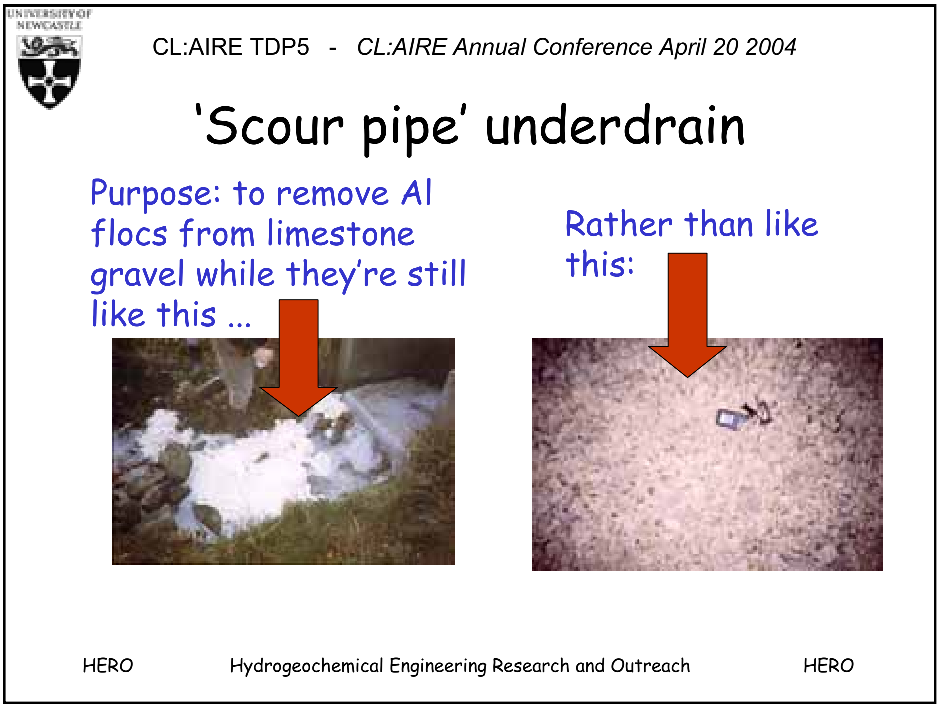

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'Scour pipe' underdrain

Purpose: to remove Al flocs from limestone gravel while they're still like this ...

Rather than like this:

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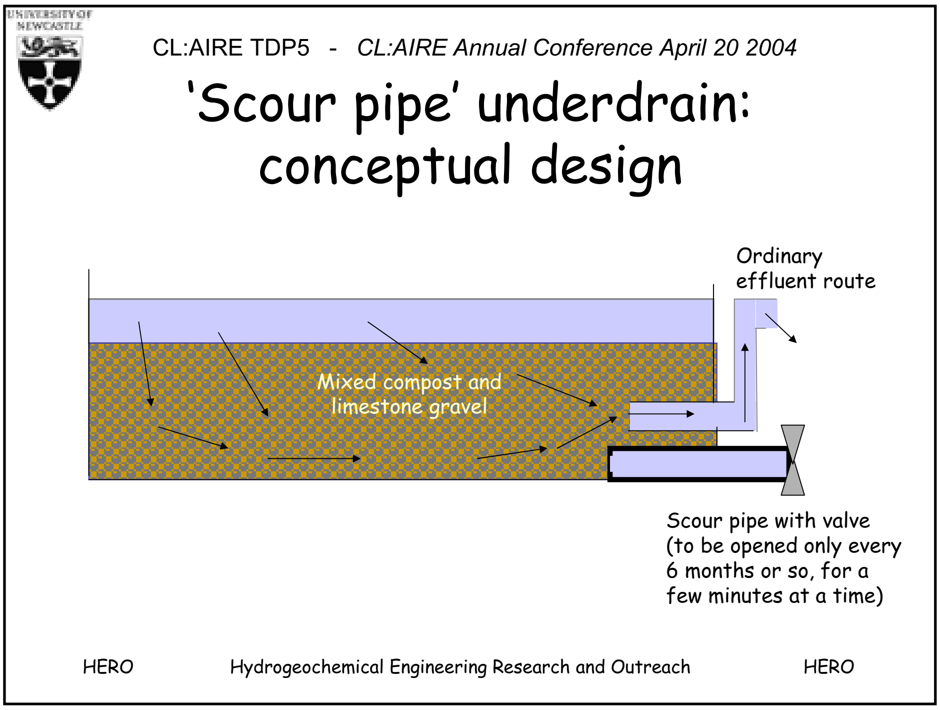

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'Scour pipe' underdrain: conceptual design

Mixed compost and limestone gravel

Ordinary effluent route

Scour pipe with valve (to be opened only every 6 months or so, for a few minutes at a time)

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Flexi-adjustable RAPS outlet pipe for head-control / scouring

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Secure monitoring facilities

- Each inlet and outlet structure is housed in a locked burglar-unfriendly chamber, designed with plinths to accommodate auto-samplers and flow logging devices
- At four points in each of the RAPS units, clusters of triple-level piezometers have been installed, uniquely routed to access points along pond perimeter

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Monitoring chamber under construction

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Monitoring chamber in use

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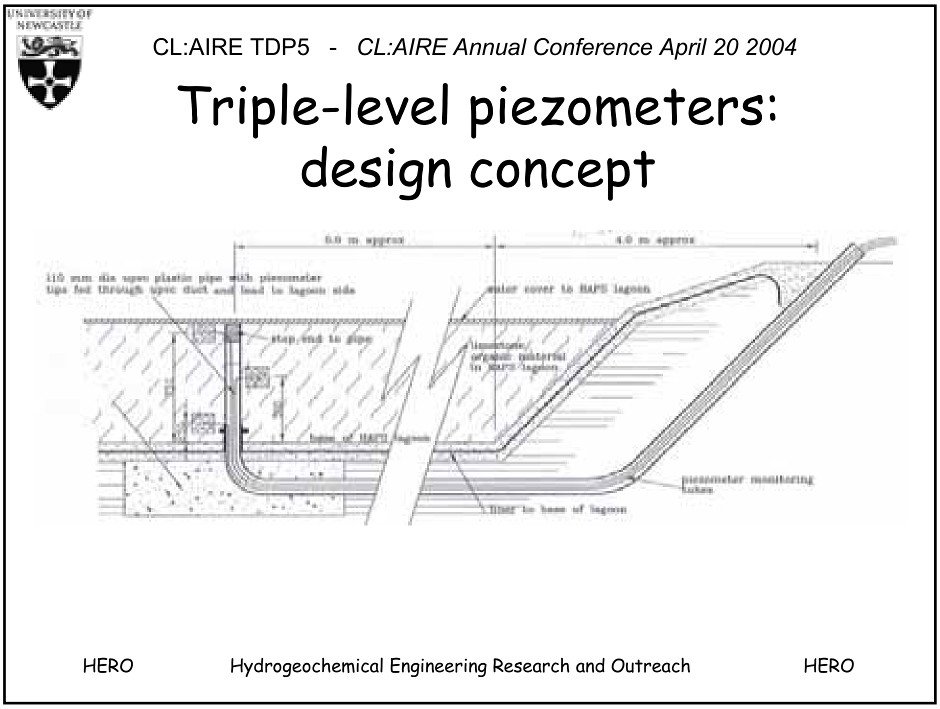

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Triple-level piezometers: design concept

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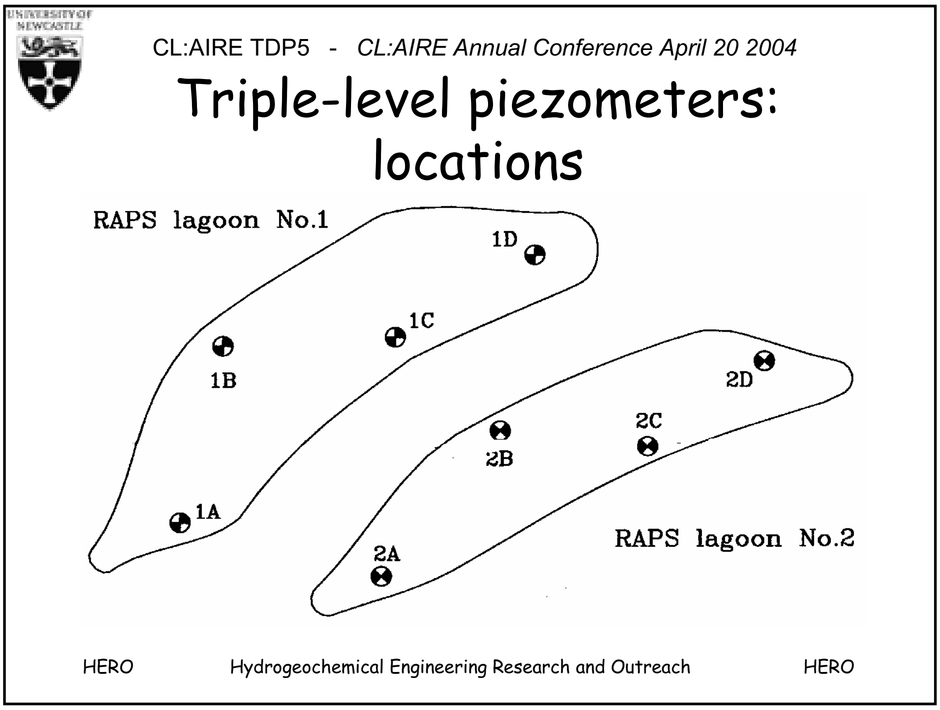

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Triple-level piezometers: locations

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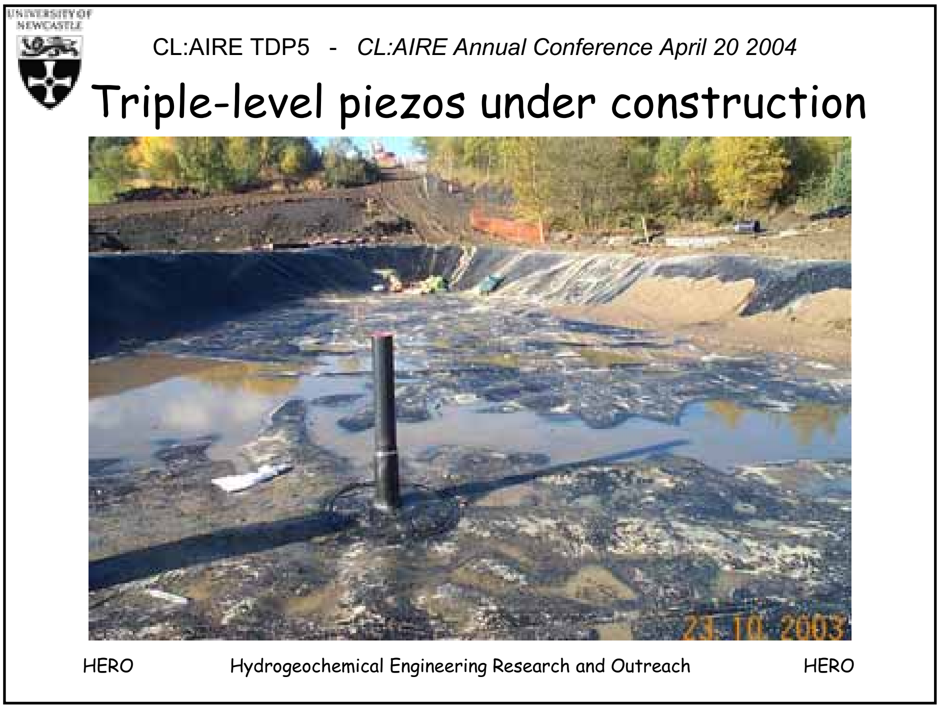

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Triple-level piezos under construction

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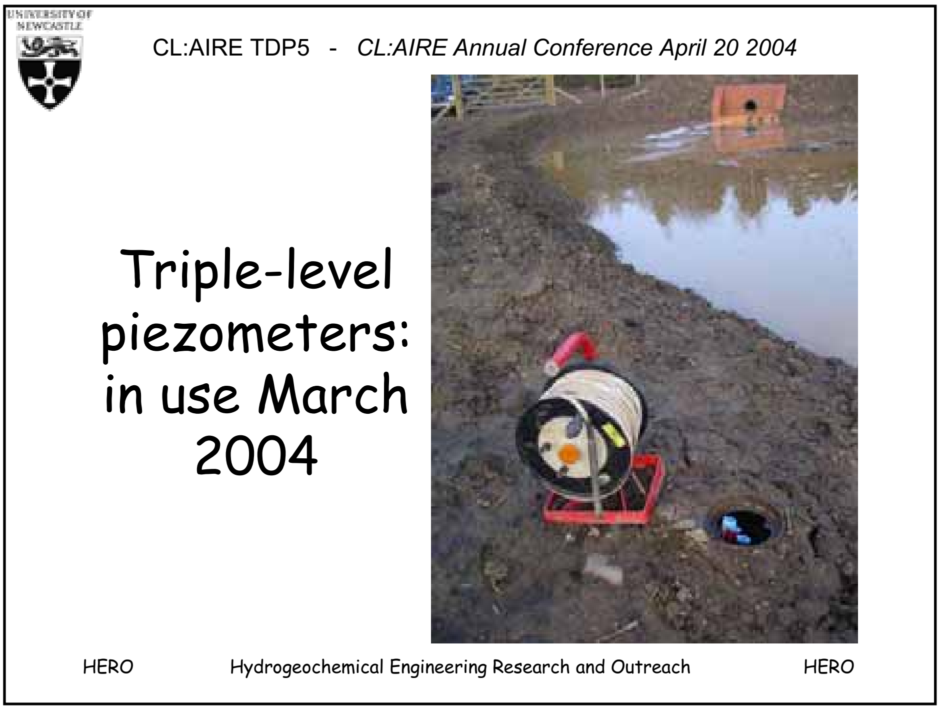

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Triple-level piezometers: in use March 2004

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Early system performance (winter 2003-04)

- Influent pH as low as 3.6; effluent pH > 6.6
- Aluminium always lowered below detection limits during flow through RAPS units
- RAPS always add 90 – 270 mg/l as $CaCO_3$ of alkalinity to water
- Net acidity removal rates of both RAPS units average 247 mg/l as $CaCO_3$
- Area-adjusted acidity removal rates 20 to 40 $g/d/m^2$

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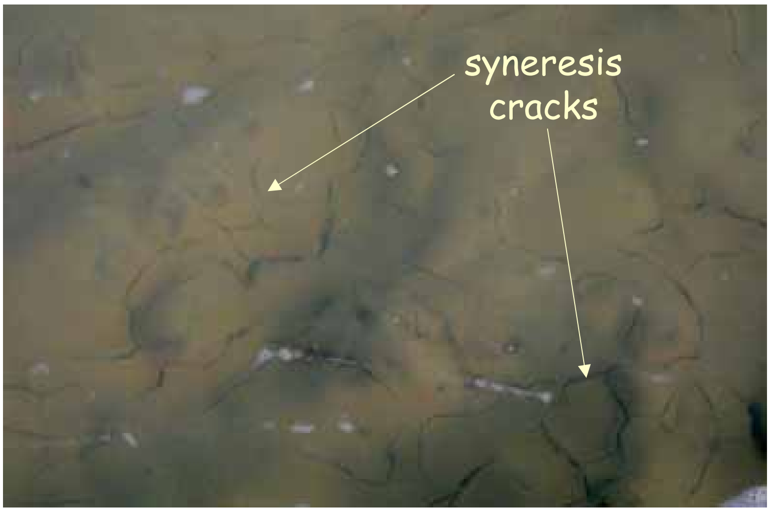
Al accumulation on surface of RAPS 2



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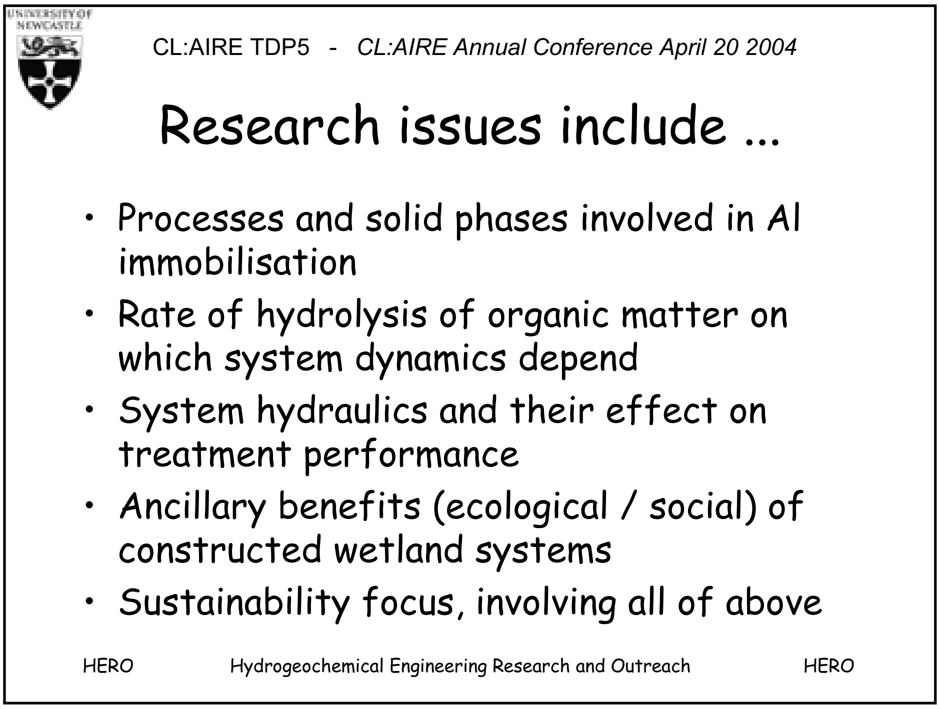

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Research issues include ...

- Processes and solid phases involved in Al immobilisation
- Rate of hydrolysis of organic matter on which system dynamics depend
- System hydraulics and their effect on treatment performance
- Ancillary benefits (ecological / social) of constructed wetland systems
- Sustainability focus, involving all of above

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Research activities

- Bowden pilot study within major EU FW5 project 'PIRAMID' (www.piramid.org)
- EPSRC/BBSRC LINK Biorem 4 project 'ASURE': Univ of Newcastle, Univ Wales Bangor, Rio Tinto, Scottish Coal, IMC Ltd (£920K)
- EPSRC Platform Grant: Generic Unifying Concepts in Wastewater Treatment Design
- **CoSTaR**: CL:AIRE national facility and now also an European Commission FP6 'International Access Infrastructure' (May '04 – April '08)

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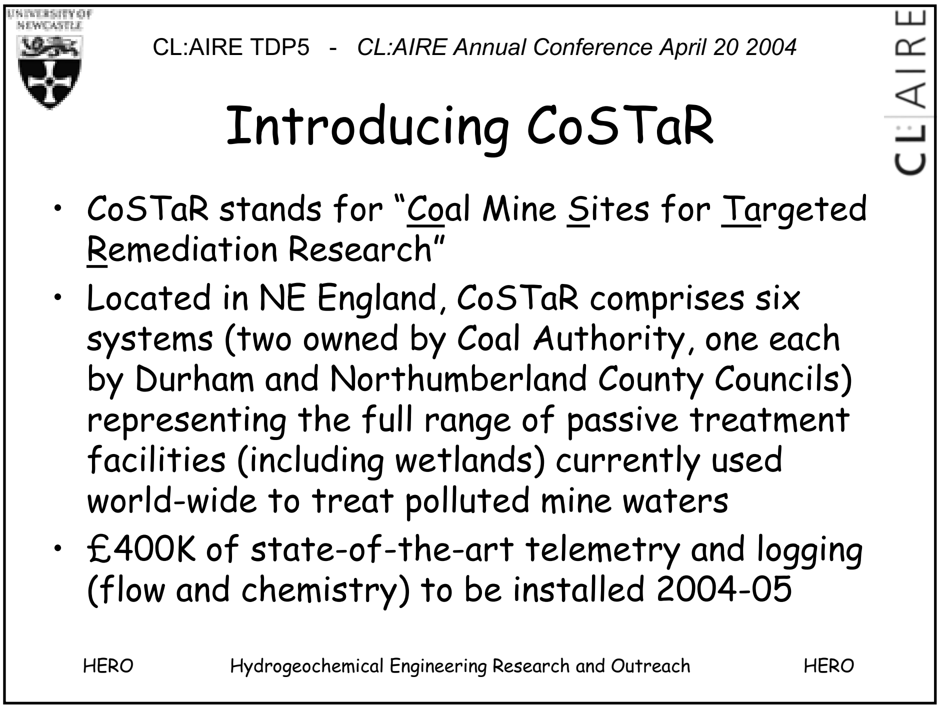

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Introducing CoSTaR

- CoSTaR stands for "Coal Mine Sites for Targeted Remediation Research"
- Located in NE England, CoSTaR comprises six systems (two owned by Coal Authority, one each by Durham and Northumberland County Councils) representing the full range of passive treatment facilities (including wetlands) currently used world-wide to treat polluted mine waters
- £400K of state-of-the-art telemetry and logging (flow and chemistry) to be installed 2004-05

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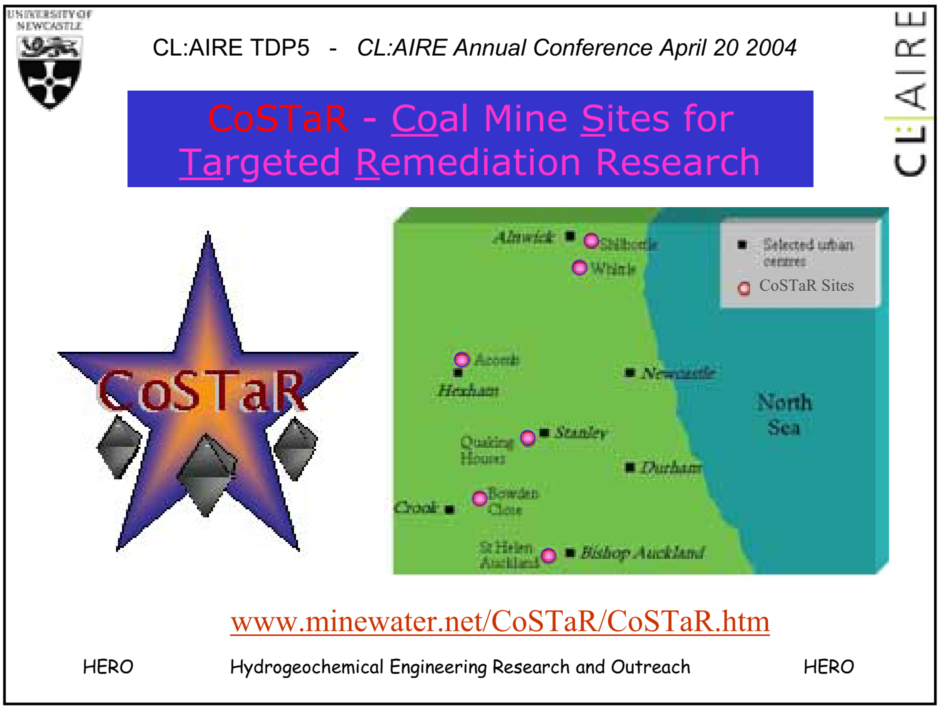

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CoSTaR - Coal Mine Sites for Targeted Remediation Research

www.minewater.net/CoSTaR/CoSTaR.htm

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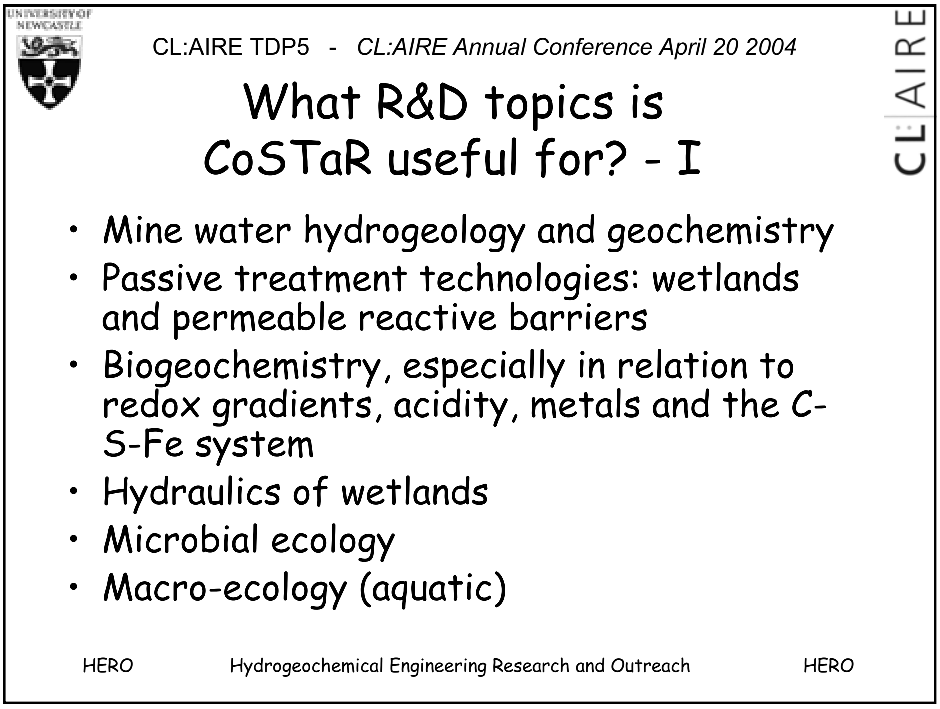

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What R&D topics is CoSTaR useful for? - I

- Mine water hydrogeology and geochemistry
- Passive treatment technologies: wetlands and permeable reactive barriers
- Biogeochemistry, especially in relation to redox gradients, acidity, metals and the C-S-Fe system
- Hydraulics of wetlands
- Microbial ecology
- Macro-ecology (aquatic)

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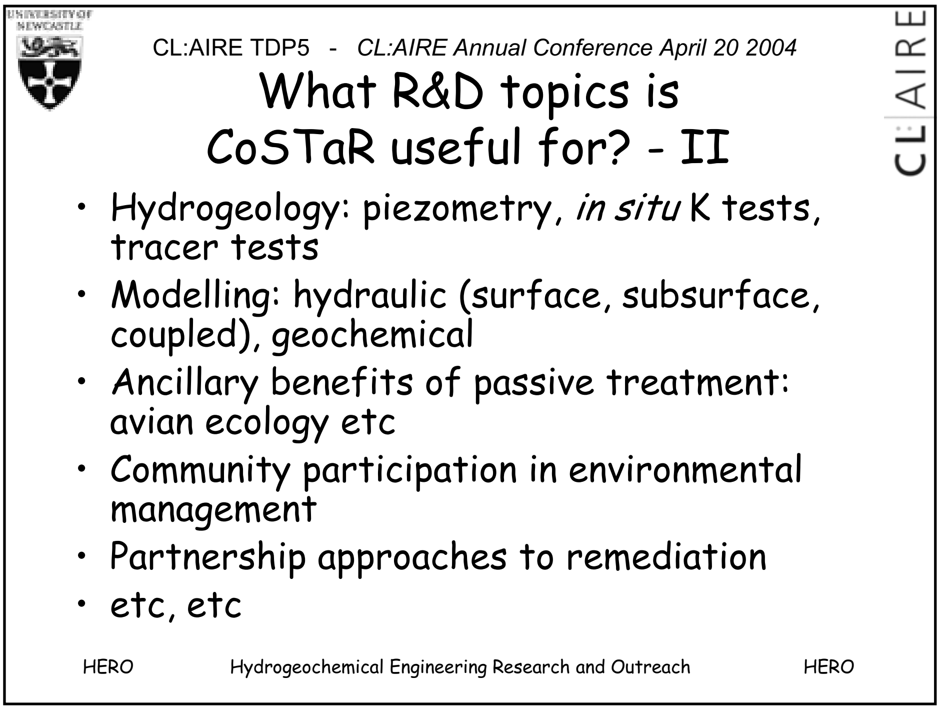

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What R&D topics is CoSTaR useful for? - II

- Hydrogeology: piezometry, *in situ* K tests, tracer tests
- Modelling: hydraulic (surface, subsurface, coupled), geochemical
- Ancillary benefits of passive treatment: avian ecology etc
- Community participation in environmental management
- Partnership approaches to remediation
- etc, etc

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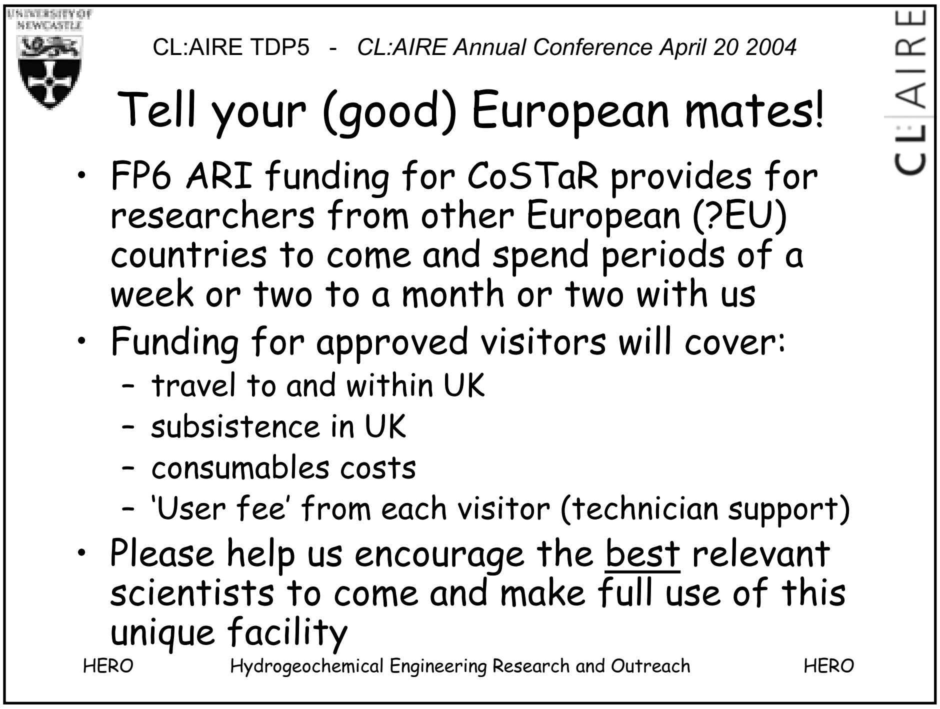

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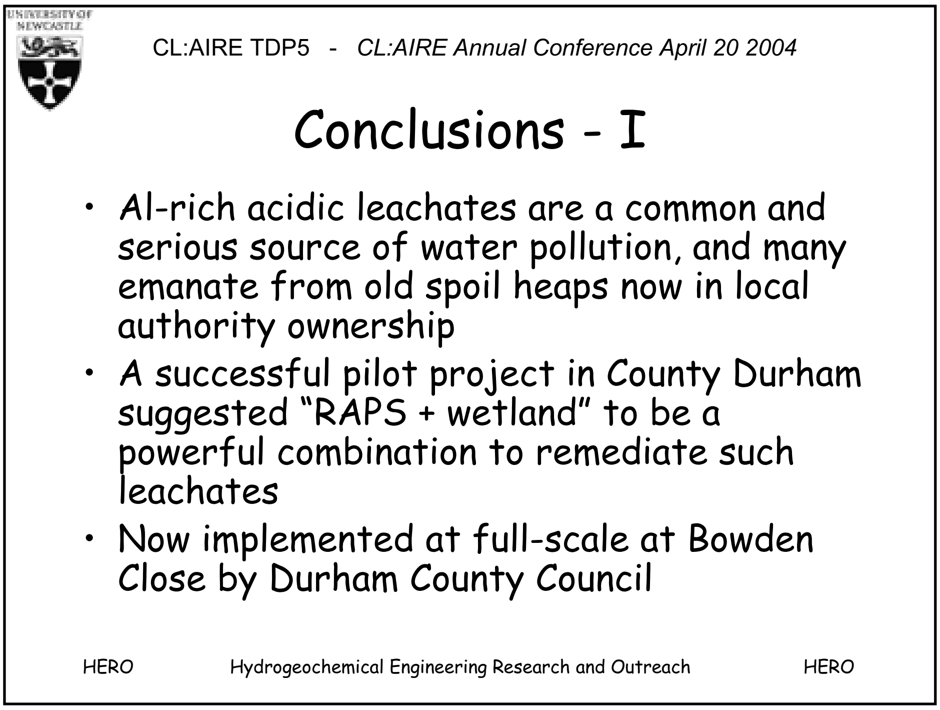

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Conclusions - I

- Al-rich acidic leachates are a common and serious source of water pollution, and many emanate from old spoil heaps now in local authority ownership
- A successful pilot project in County Durham suggested "RAPS + wetland" to be a powerful combination to remediate such leachates
- Now implemented at full-scale at Bowden Close by Durham County Council

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Conclusions - II

- Full-scale system now undergoing final commissioning (adjustment of hydraulic gradients across RAPS 2; reeds planting in aerobic wetland May-June 2004)
- Will be fully documented as CL:AIRE TDP5
- New system includes unparalleled research infrastructure and forms part of the major CL:AIRE CoSTaR facility
- FP6 funding available for the use of colleagues from all over Europe – please spread the word!

Acknowledgements

- Pilot system *dramatis personae:*
  - Neal McCay (Durham CC), James Coulson, Paula Canteli, Adam Jarvis, Lesley Batty (N'cle Univ), CDENT (funding)
- Full-scale system:
  - Conceptual design: Univ of Newcastle
  - Detailed design by site owners Durham County Council; funding from SCA
  - Construction: Balfour Beatty
  - Research funding BOC Foundation and CL:AIRE
- Special thanks to Newcastle colleagues: Patrick Orme, Andy Aplin, Daniel Fabian

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Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

A full-scale reducing and alkalinity-producing system (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham.

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ABSTRACT

Leachates generated by old colliery spoil heaps can pose significant risks to ecosystems, drinking water supplies and agricultural / commercial uses of surface waters. At Bowden Close in County Durham, investigations have been underway since 1999 into low-cost, environmentally-integrated methods for neutralising the acidity of, and removing ecotoxic metals from, such spoil leachates and similar drift mine drainage waters. Successful pilot-scale field tests (undertaken by the University of Newcastle and Durham County Council in 1999-2001) showed that it is feasible to passively treat Al-rich acidic leachates using subsurface flow biogeochemical reactors containing a mixture of compost and limestone. These so-called 'Reducing and Alkalinity-Producing System' (RAPS) improve water quality by the combined action of bacterial sulphate reduction and calcite dissolution. A full-scale passive treatment system based on this approach was constructed in the autumn of 2003, and full commissioning will be completed in the summer of 2004. The full-scale system incorporates two RAPS units, specifically designed to optimise Al^{3+} removal, and a polishing aerobic wetland (reedbed). Significant logistical and financial support from CL:AIRE, the BOC Foundation and the University of Newcastle's SRIF2 Earth Systems Laboratories initiative is facilitating the inclusion in this new system of unparalleled monitoring facilities. Early performance data from the new system, even before commissioning is finished, are very encouraging: pH rises from as low as 3.6 to as high as 7.6 as the polluted waters pass through the system. Net acidity removal (i.e. acidity removed plus alkalinity added) reaches nearly 250 mg/l as $CaCO_3$. Al concentrations fall from ≤ 22 to <0.5 mg/l. Fe drops from around 40 mg/l to < 10 mg/l; after the aerobic wetland is planted with *Typha latifolia* later this year, significantly lower final Fe concentrations (perhaps below 2 mg/l) are anticipated.

INTRODUCTION

The site of the former Bowden Close Colliery lies in the vicinity of the village of Helmington Row, in southwestern County Durham (Figure 1). After the colliery closed in the 1960s, the site was taken into the possession of Durham County Council, who proceeded to restore it according to the best practice of the period. Mine entrances were sealed and buried, derelict buildings were demolished and the voluminous spoil heaps which dominated the site were re-profiled and vegetated. The end result was a popular golf course in a pleasant rural setting.

As in many other reclamation schemes implemented prior to 1990, subsurface contamination issues were not a key driver in the original restoration scheme. However, by the end of the 1990s, Durham County Council were re-evaluating the Bowden Close site on account of two separate issues of ground contamination and associated pollutant seepages to the surface environment:

(i) Tar pollution arising from two large buried tanks, associated with the coke works which formerly occupied the southern portion of the Bowden Close site, and
(ii) Acidic, metalliferous waters, arising from spring-like features and land drains within the site, which severely polluted the adjoining Willington Burn.

A large-scale dig-and-dump operation implemented in 1999 effectively dealt with the tar pollution issue. During this operation, research was undertaken which established the feasibility of using biodiesel as a reagent to render recalcitrant tars amenable to bioremediation (Taylor and Jones, 2001).

The present paper concerns the steps taken to provide a long-term passive solution to the problems arising from the acidic metalliferous drainage on this site. Although this programme was initiated in 1999, it is only in 2004 that final completion of all of the required actions is finally within sight. This aspect of the Bowden Close remediation scheme was adopted by CL:AIRE as Technology Demonstration Project No 5 (TDP5), on account of a number of aspects of the scheme which are novel (Younger 2002). These include the specific targeting of passive technologies at aluminium removal, and the use of wholly mixed substrates in a subsurface flow bioreactor.

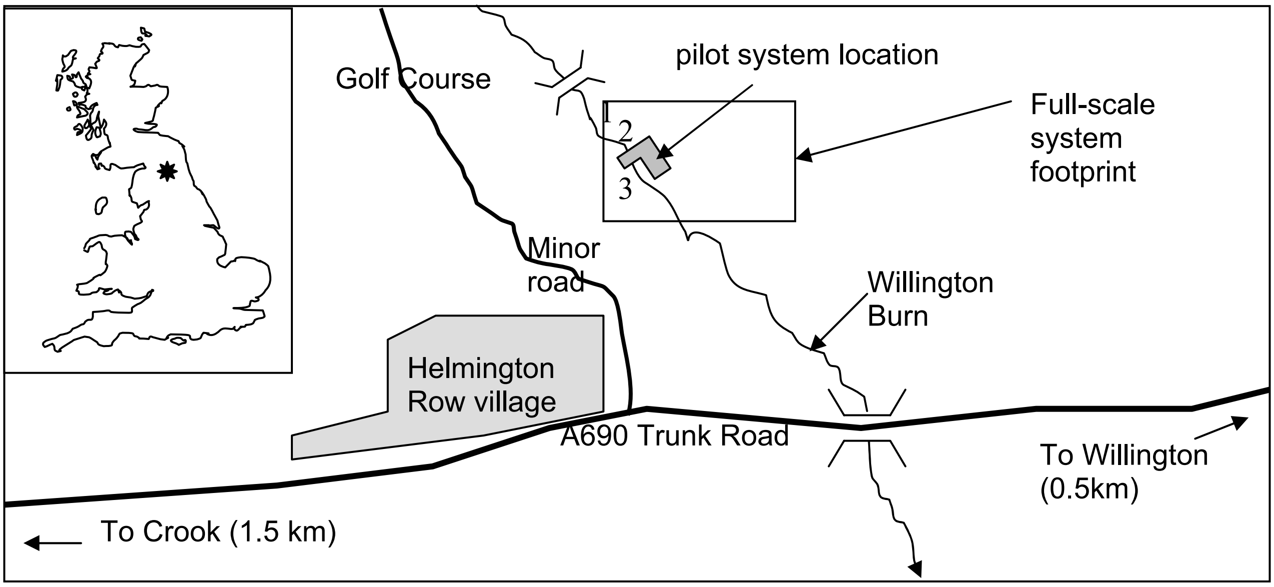


Figure 1 - Location of the Bowden Close (TDP5) passive mine water treatment site. The numbered points 1 - 3 are the three polluted discharges discussed in the text.

ACIDIC DRAINAGE AT BOWDEN CLOSE

The first published study of the acidic drainage at Bowden Close (Younger, 1995) revealed the waters to be very acidic (pH 3 - 4), with high concentrations of Fe and Al. Subsequent biological surveys of the receiving watercourse showed these polluted waters to be causing severe ecological damage (Jarvis and Younger, 1997). Site characterisation studies in 1998/99 revealed that there are actually three distinct, perennial discharges of acidic mine drainage at this site (as summarised in Table 1).

Discharge No 1 is the furthest upstream of the three perennial discharges. (Although minor ferruginous seepages do sometimes occur further upstream, these are not quantitatively significant). The No 1 discharge originally emerged from a 0.5m diameter concrete drainage pipe on the true left bank of the Willington Burn, some 50m downstream of the grassy "bridge" over the Burn within the golf freeway. Although this discharge is perennial, in the height of summer and into the mid-autumn the flow can drop to a very low rate (around 0.03 l/s). During the construction of the full-scale passive system in the autumn of 2003, it was discovered that this discharge actually originates from an old mine access drift driven in the Harvey Seam, which lies only a few feet below ground at this point. A new connection into this drift was constructed, and the entire discharge captured and carried in a pipeline to the full-scale passive system.

Discharge No 2 originally entered the Willington Burn from its left bank some 25m downstream of the No 1 discharge. The source of this discharge has been observed to vary seasonally. At times it has dried up completely. At times when it is flowing at a low rate (< 0.1 l/s), the source of polluted water appears to be in a hollow amidst the stand of conifers which line the eastern flank of the Burn. This hollow is now known to be the collapsed remains of the portal of the same drift which gives rise to the No 1 discharge. During the laying of the No1 discharge pipeline a "water gate" (i.e. a small tunnel constructed to lead water out of the access drift) was unearthed, leading south-westwards from the location of the old drift portal towards the Burn. This carried a small seepage of polluted water, which was therefore diverted into the No 1 discharge pipeline. It is believed that all water formerly the seeping through the drift portal will now be captured in this manner, so that the hollow at the former portal will likely not flow at all in future. During wetter periods, the water entering the Willington Burn at the 'Discharge No 2' location commences rather higher up the site, as spoil leachate flowing from a small rill cutting spoil which underlies the eastern golf course greens. This is so acidic (pH < 2.5) that it is not visibly polluted until it mixes with less polluted water a short distance downstream, where pH rise to > 4 and both ochre and aluminium foam become apparent in the channel. The diversion of this water into the full-scale passive treatment system was being finalised at the time of writing. Table 1 summarises the characteristics of the No 2 discharge as measured in the spring and summer of 1999.

Discharge No 3 is the largest and most heavily polluted of the three main discharges, and it lies at the most downstream position of the three. Unlike the other two discharges, No 3 arises on the right bank of the Willington Burn. It is the point source previously sampled by Younger (1995), and it corresponds to the "Helmington Row A" discharge described in the Coal Authority's survey of 1996. It is usually conspicuously aluminium rich, depositing much white froth in and on the banks of the Willington Burn. It is believed to be spoil toe drainage from a perched water table within the spoil on the western bank of the Burn.

Table 1. Mean flow and selected hydrochemical parameters (total concentrations) for the three mine site drainage discharges at the abandoned Bowden Close Colliery, Co Durham.

Discharge No.	*Mean flow rate (l/s)*	*Fe (mg/l)*	*Al (mg/l)*	*Zn (mg/l)*	*Alkalinity (mg/l as $CaCO_3$)*	*SO_4 (mg/l)*	*pH*
1	0.25	30	10	0.3	10	300	5.5
2	0.2	8	2	0.1	50	140	6.7
3	3.3	80	50	3	0	1530	4.0

BOWDEN CLOSE PILOT SCHEME

This system has been described in detail by Younger (2000, 2002) and Younger *et al.* (2003), so only a short summary is presented here. The Bowden Close pilot passive treatment system was constructed in the late summer and autumn of 1999 (Figure 2), and was operated until February 2001 (when further site work became impossible due to the Foot-and-Mouth Disease countryside access restrictions). The pilot system comprised a single RAPS unit followed by a small aerobic pond. (See Section 5 for definitions and explanations of these two unit passive treatment processes). Due to the late date of construction, which rendered the planting of reeds impractical, the small aerobic pond was vegetated with transplanted common rush (*Juncus effusus*). Discharges 1 and 2 were both fed into this system, which thus received a mean inflow of some 0.45 l/s of water with mean concentrations of 10 mg/l Fe and 2 mg/l Al. Influent alkalinity varied from zero to 68 mg/l.

System performance was impressive, with Fe concentrations being lowered to between 1 and 0.1 mg/l and Al concentrations to less than 0.3 mg/l (and often less than 0.01 mg/l), with effluent pH being consistently in excess of 7, and usually in the range 7.5 to 8.7. Alkalinity generation in the RAPS was particularly striking, with as much as 180 mg/l (as $CaCO_3$ equivalent) being imparted to the waters as they passed through the system (average alkalinity generated: 107 mg/l as $CaCO_3$). Overall the system proved capable of removing 25 grammes of acidity (as $CaCO_3$ equivalent) per m^2 of RAPS surface area per day, which is comparable with rates reported from systems in warmer climate settings in the eastern USA (Watzlaf *et al*. 2000).

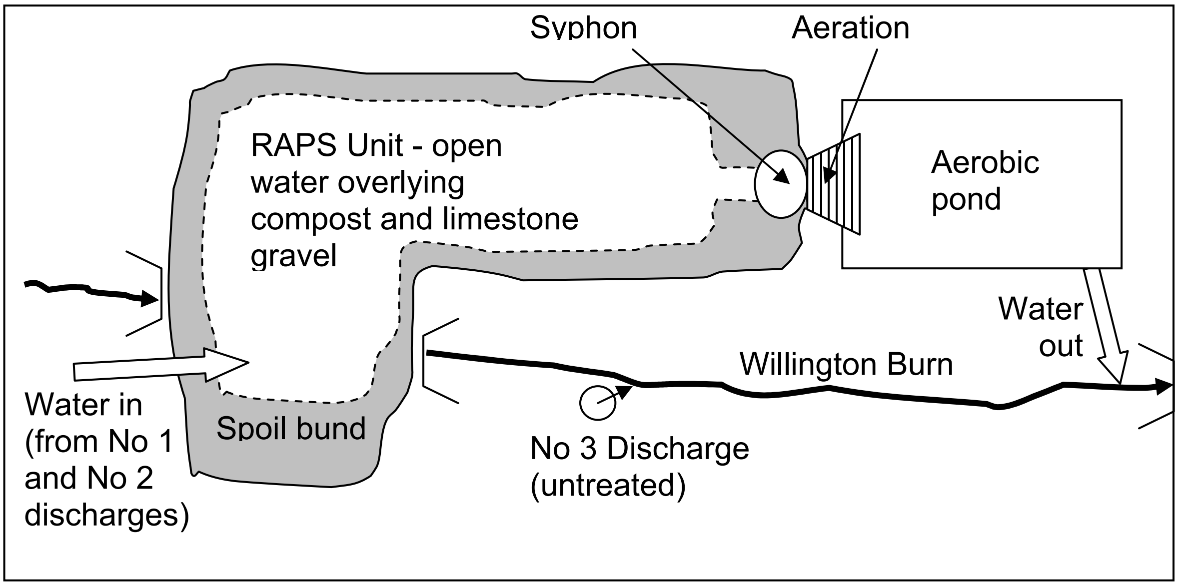


Figure 2 - Sketch plan of the Bowden Close pilot passive treatment system, which operated from 1999 to 2001.

MOVING TO FULL-SCALE

Following on from the success of the pilot project, Durham County Council were keen to move onto installation of a full-scale passive system at Bowden Close. Funding for the system was obtained by the Council by means of the Supplementary Credit Approval mechanism, sanctioned by DEFRA. Although SCA funding was originally approved for spending in financial year 2000-2001, scheduling of other work planned by the Council meant that construction had to be held over to FY 2001-2002. In the event, the Foot and Mouth Disease outbreak prevented construction of the system in that year. By the time the plans came to be revisited, changes had occurred in the mode of implementation of Part IIA of the Environmental Protection Act 1990 and in the manner in which the Council had to deal with delivery of capital works. These changes occasioned further delays in getting approval for a final design which could be constructed on behalf of the Council by the framework partnering company, Balfour Beatty.

One of the most significant challenges to be overcome was the location of the full-scale passive system. Whereas the pilot passive system captured only the No 1 and No 2 discharges, it was always essential that the full-scale system capture all three discharges. Given the locations of the three discharges, achieving this goal was a significant challenge. For a passive system to be successfully constructed, it was essential that it be located on a site which:

a. is sufficiently spacious to allow full passive treatment of the water to preferred discharge consent standards.
b. lies topographically lower than the three discharge points, but not so far from the discharges as to demand piping untreated water over large distances.
c. is not so steep that cut-and-fill activities would be too difficult to achieve.
d. has soil conditions consistent with minimal geotechnical stabilisation requirements (which favoured building on native glacial till rather than on the rather treacherous colliery spoil which underlay the pilot plant site).
e. does not already have high landscape value (e.g. mature woodland).

No parcel of land could be identified which met all of the above criteria. However, to the east of the Willington Burn a parcel of low-lying arable farmland was identified which complied with all of the above criteria with the exception of (a). This land was rather prone to water-logging, and hence was often unproductive agriculturally. Negotiations to purchase this land were successful. To attempt to compensate for its lack of full compliance with criterion (a) above, it was simply resolved that system design would be tailored so as to achieve as high a degree of treatment as possible in the space available. The design which was developed to achieve this is described in the following section.

It was not until mid-summer 2003 that the construction of the system at Bowden Close finally received a green light. Knowing from experiences of the pilot scheme just how difficult this site can be to work in wet weather, all concerned were anxious about the potential difficulties of completing the scheme before the end of the financial year. However, fortunes were favourable as one of the driest autumns on record ensued, allowing completion of the earthworks before the rains finally began to fall in earnest in November 2003. Nevertheless, with construction occurring in the second half of the year, it was not possible to plant up the final wetland in 2003, and this task is now scheduled for completion in late May / early June 2004.

FORM AND FUNCTION OF THE FULL-SCALE PASSIVE SYSTEM

The conceptual design of the full-scale system was undertaken by the author, and it was worked up into a detailed design by staff of Durham County Council. The layout of the system is summarised in Figure 3. The basic logic of the system is to use anaerobic processes to neutralise the mineral acidity of the waters, followed by aerobic processes to 'polish' the concentrations of key contaminants (Fe, Al, Mn and Zn) prior to final discharge to the Willington Burn. The anaerobic processes are deployed within subsurface flow systems known as 'RAPS units', in which anoxic conditions are achieved by the oxygen-stripping action of organic compost (based on horse manure and straw in this case). Calcite dissolution is also effected under these anaerobic conditions, which ensures that all dissolved iron is converted to the ferrous form (Fe^{2+}), avoiding the problems of blinding of limestone clasts which occurs when iron is in the oxidised ferric form (Fe^{3+}). As is evident from Figure 3, the system is designed such that Discharge Nos 1 and 2 are directed into 'RAPS Lagoon No 1' via inlet chamber IC 01, with Discharge No 3 being passed into a RAPS of its own ('RAPS Lagoon No 2') via inlet chamber IC 02. The effluents from both RAPS units are subsequently mixed in a shared aerobic wetland (reed-bed) prior to final discharge to the Willington Burn via outlet chamber OC 03. Mine water leaving the RAPS units is expected to have a circum-neutral pH, which favours extremely rapid abiotic oxidation of Fe^{2+} to Fe^{3+}. The latter then hydrolyses rapidly to form ferric hydroxide (ochre). Any residual aluminium in the RAPS effluent will similarly hydrolyse at a very rapid rate. Mn^{2+} will also oxidise to Mn^{4+}, and precipitate as MnO_2 (pyrolusite) within the aerobic wetland. While some removal of Zn can be expected to occur within the RAPS units, further Zn removal can be anticipated in the reedbed, principally by means of sorption onto freshly precipitated ochre.

The design of the RAPS units at Bowden Close incorporates two novel features. The first is manifest in the nature of the reactive substrate in the Bowden Close RAPS (Figure 4), which is a thorough mixture of limestone clasts and compost. This differs markedly from the original RAPS design of Kepler and McCleary (1994), in which a discrete layer of limestone gravel underlies a layer of compost. Replacing this two-layer design with a mixed limestone / compost bed overcomes the following two drawbacks of the original design:

(i) throttling of the flow through the system by the limited permeability of the compost layer (which is typically some orders of magnitude lower than that of the limestone gravel layer), and

(ii) the public safety hazard represented by the presence of more than 0.5m of saturated organic matter as the surface layer.

This design development has been analysed in further detail in recent publications, which point to evidence in its favour obtained during both lab trials (Amos and Younger 2003) and during the operation of the Bowden Close pilot system (Younger 2002).

The second novelty of the Bowden Close system lies in the design of the hydraulic control at the ends of each of the RAPS units. These have been designed such that all of the water leaving the base of the compost/limestone bed is collected in fixed pipework which ends in a flexible hose suspended on chains (within a locked chamber). Not only does this make the system far easier to adjust in response to changing flows and RAPS substrate permeabilities, but it also allows for periodic dropping of the pipes to the base level of the RAPS, facilitating

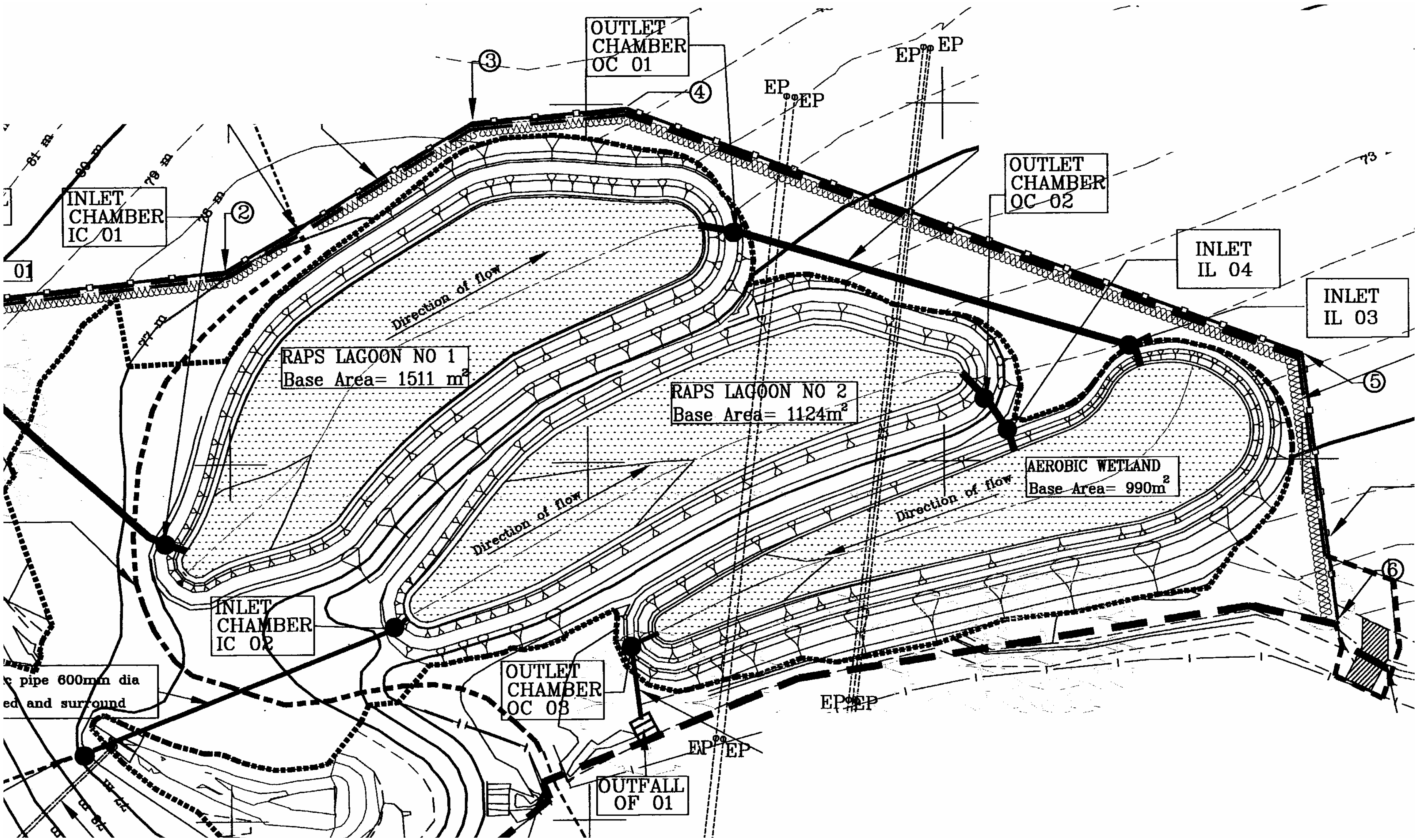


Figure 3 - Layout of the full-scale passive treatment system constructed in the autumn of 2003 at Bowden Close, Co Durham.

occasional 'scouring' of the substrate by imposing a very steep hydraulic gradient across the RAPS. This in turn should allow mobilisation of aluminium from within the pore space of the RAPS, helping to prolong the life of the reactive substrate (cf Kepler and McCleary 1997). This is especially useful in relation to RAPS 2, which receives very aluminous water.

It is also worth noting that, while RAPS 1 is fitted with an artificial liner (a HDPE membrane), RAPS 2 is unlined. The reason for this contrast was that RAPS 1 is partly dug into *in situ* clay, and partly built-up from backfilled clay removed from the RAPS 2 basin. As compaction of backfill to an uniformly low permeability is difficult to quality control on such a large structure, and as repairs would be difficult after substrate had been emplaced, it was decided that an artificial liner was justified. For RAPS 2, however, the basin is *only* excavated, not built-up. The low permeability of the undisturbed glacial till into which the RAPS 2 basin was excavated is sufficient to retain all water without further lining. Given that this RAPS receives the worst of the three discharges, and is therefore likely to need maintenance (substrate renewal) more regularly than RAPS 1, the absence of an artificial liner is a great benefit, as this means that substrate can be removed by straightforward digging without any need for costly precautions to avoid puncturing an artificial liner.

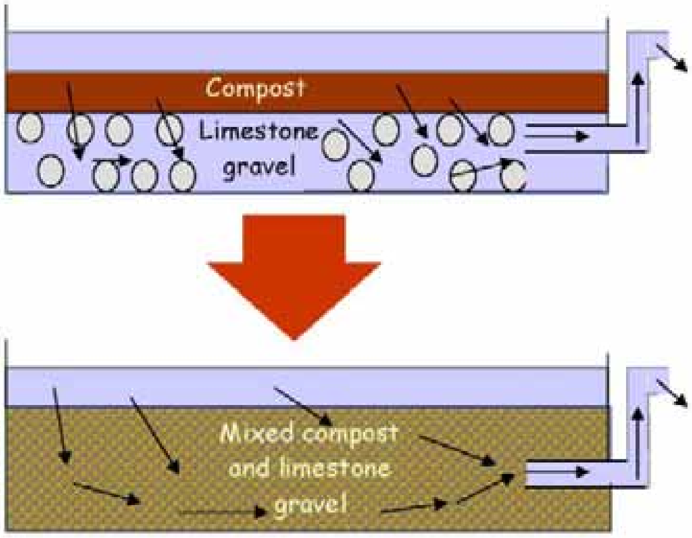


Figure 4 - Schematic cross-sections illustrating the shift in design concept from the layered RAPS design, as originated by Kepler and McCleary (1994) (top) to a fully mixed substrate, as used in the full-scale passive system at Bowden Close (bottom).

Just as significant as these process design innovations are the high-quality monitoring facilities which were incorporated in the system design. These features were made possible through significant financial support from CL:AIRE and the BOC Foundation. Secure, locked access chambers have been installed at the inlet and outlet of each of the RAPS units and of the aerobic wetland. These chambers have been designed to accommodate auto-samplers, multi-parameter water quality sondes and flow monitoring equipment. In addition, within the reactive substrates of both RAPS units triple-level piezometer clusters have been installed in accordance with an unique, novel design (Figure 5). Four such clusters have been incorporated into each of the two RAPS units (Figure 5b), giving eight positions in all at which it is possible to determine changes in hydraulic head and water quality over depth, as the water flows through the RAPS substrate.

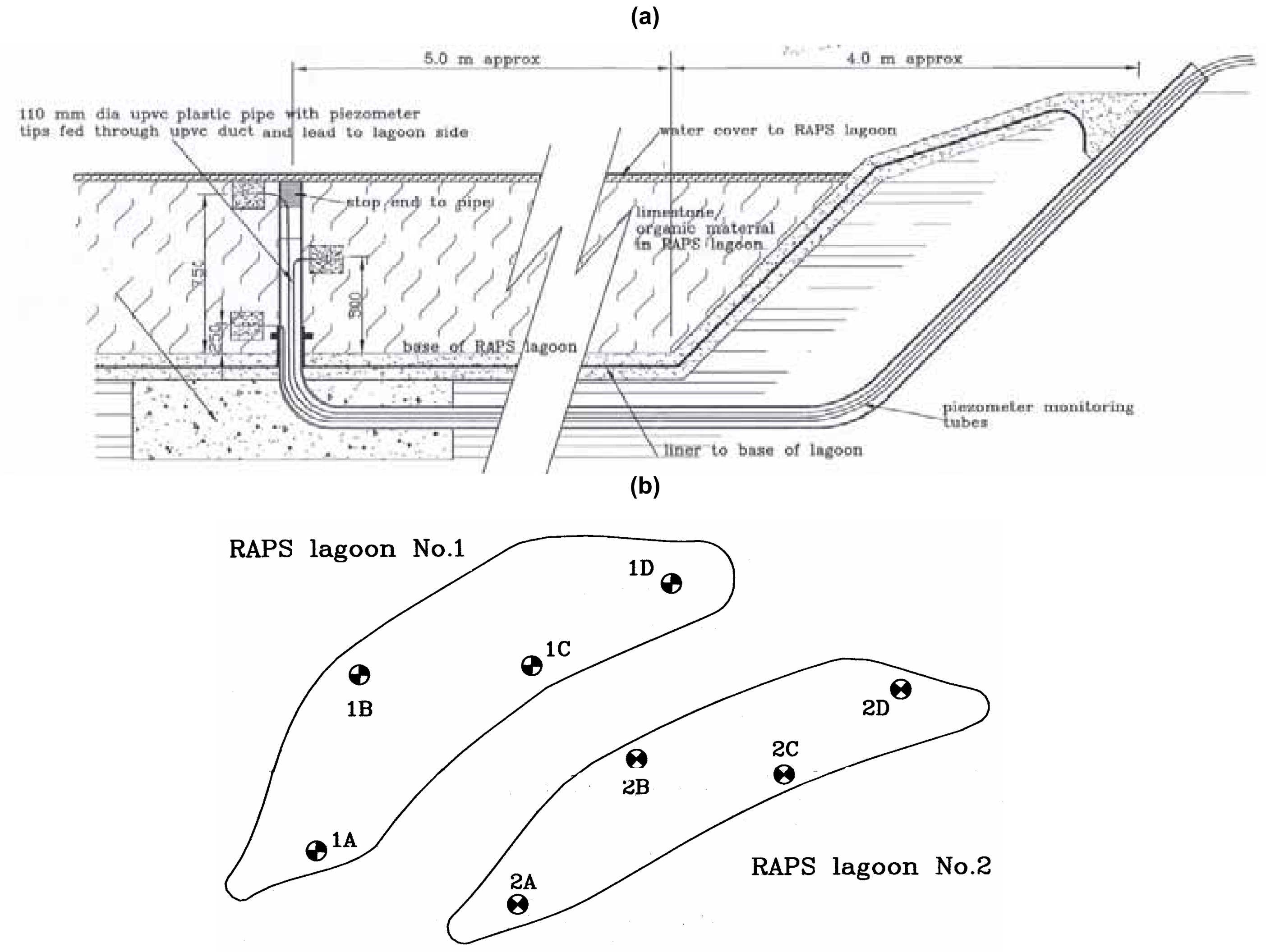


Figure 5 - Triple-level piezometers in the Bowden Close RAPS units. (a) cross-section through the centre and bund of a RAPS unit showing the mode of construction (b) plan showing locations of triple-level piezo clusters within the RAPS units.

With these unique monitoring facilities in place, the scope for data capture and transmission is now planned to be further augmented by substantial additional investment in FY 2004-2005 from the University of Newcastle's SRIF2 spend, under the auspices of their new "Earth Systems Laboratories" initiative. This will provide the means for real-time transmission of flow and chemistry measurements to the University of Newcastle campus, enabling far greater observation of this system than has yet been achieved at any similar passive system anywhere in the world. At the time of writing, equipment to be installed in these monitoring chambers is under procurement, and is expected to be deployed during the summer of 2004.

EARLY PERFORMANCE OF FULL-SCALE SYSTEM

As the Bowden Close system is not yet fully commissioned (adjustment of the head gradient across RAPS 2 is still in progress, and the aerobic wetland will not be planted with reeds until June 2004), it is still rather early to be discussing the performance of the system. Furthermore, in any discussion of system performance now or in future it is important to note that the limited availability of land at the site inevitably led to under-sizing of the RAPS and the aerobic wetland. The contrast between the ideal areas of the system components and their actual areas is highlighted in Table 2 below. While the disparity is modest for RAPS 1, the actual area of RAPS 2 is only about a quarter of the size that would have ideally been preferred.

Table 2 - Ideal versus actual areas of component passive treatment units in the Bowden Close passive treatment system

Element of system …	**Ideal area[a] (m^2)**	**Actual area[b] (m^2)**
RAPS 1	1728	1511
RAPS 2	4350	1124
Aerobic wetland	1300[c]	990

[a] as suggested by loading-based design calculations following the recommendations of Younger *et al.* (2002)
[b] see Figure 3. [c]Assumes a flow-weighted average of 15 mg/l Fe coming from RAPS 1 and RAPS 2.

Given the grounds for caution indicated by Table 2, the early performance data from the new system (in advance of final commissioning) are extremely encouraging. Table 3 summarises changes in key quality parameters as the water flows through the system. It should be noted that the fact that some parameters appear to increase in the aerobic wetland above the values leaving the RAPS (e.g. for aluminium) is simply due to the fact that, with commissioning as yet incomplete, some overflow of untreated water from RAPS 2 to the wetland is still occurring. (Initially, both RAPS 1 and RAPS 2 were overflowing, but increasing the hydraulic head across RAPS 1 solved this problem by mid-February 2004). Gradual adjustments of the RAPS 2 head control is progressively decreasing the overflow from this unit too, though at the time of writing about 50% of the influent to RAPS 2 is still overflowing. We anticipate eliminating overflow from RAPS 2 altogether by May 2004.

Even with some overflow still occurring from RAPS 2, overall system performance is extremely encouraging. Effluent pH never drops below 6.6, even though influent pH falls as low as 3.6. On no occasion has their been more acidity than alkalinity in the final discharge. Aluminium is always lowered below detection limits during flow through the RAPS units. Never less than 90 mg/l (as $CaCO_3$) of alkalinity is added to the waters by the RAPS units, and as much as 270 mg/l can be added on occasion. When acidity removal and alkalinity generation are taken into account the net acidity removal rates of both RAPS units average 247 mg/l as $CaCO_3$. In terms of area-adjusted acidity removal rates, RAPS 1 is effectively load-limited as it regularly lowers acidity to low single figures; this results in an under-stressed acidity removal rate of 5 - 9 g/d/m^2. RAPS 2 receives more acidic waters and is small in comparison to its ideal size (Table 2). It is thus very far from being load-limited, and it exhibits very high acidity removal rates, ranging from 20 to 40 g/d/m^2. It is noteworthy that these impressive performance figures relate to the winter months, when influent water temperatures within the system have fallen as low as 3.8°C, so that reaction rates can be expected to have been at their most sluggish. The overall picture is therefore highly encouraging, and the prospects for even greater performance after the final completion of commissioning are certainly favourable.

Table 3 - Water quality determined at various points in the Bowden Close System from the start of the commissioning process (still incomplete) in December 2003. All sampling and analysis undertaken by Patrick H A Orme.

Date	Sample	pH	Cond uS/cm	Alkalinity mg/l as CaCO3	Acidity mg/l as CaCO3	Sulphate mg/l	Calcium mg/l	Iron mg/l	Manganese mg/l	Aluminium mg/l
10-Dec-03	RAPS 1 inf	6.46	980	37	40	433	113	5.9	1.4	4.9
	RAPS 1 eff	7.43	1272	130	8	354	111	1.3	0.3	1
	RAPS 2 inf	5.17	1258	10	198	730	118	37.8	5.3	21.6
	RAPS 2 eff	7.26	1890	280	10	490	155	1.5	1.7	0.7
	Wetland eff	7.03	1219	70	36	421	132	10.9	2.8	2
06-Jan-04	RAPS 1 inf	6.02	911	20	47	432	118	7.6	1.2	5.6
	RAPS 1 eff	7.29	1070	108	2	309	117	0.5	0.6	<0.5
	RAPS 2 inf	6.18	641	50	57	212	62.3	12.1	1.2	5.9
	RAPS 2 eff	7.13	978	182	5	248	127	0.7	2.1	<0.5
	Wetland eff	7.02	717	71	13	176	82.5	3.9	1.0	0.7
22-Jan-04	RAPS 1 inf	4.2	980	0	101	542	116	16.2	2.1	11.8
	RAPS 1 eff	7.3	1088	115	3	344	117	0.7	1.0	<0.5
	RAPS 2 inf	5.49	950	16	130	478	102	20.8	2.7	15.8
	RAPS 2 eff	7.15	1052	162	6	358	162	1.2	2.2	<0.5
	Wetland eff	6.79	919	61	36	359	120	8.8	2.1	3
05-Feb-04	RAPS 1 inf	4.3	963	0	94	510	110	19.5	1.9	9.6
	RAPS 1 eff	7.5	961	128	4	278	117	1	1.1	<0.5
	RAPS 2 inf	6.05	847	35	101	400	95	20.5	2.2	10.8
	RAPS 2 eff	7.33	926	178	7	292	141	1.7	2.4	<0.5
	Wetland eff	7.18	787	52	25	311	105	9.6	1.8	0.8
18-Feb-04	RAPS 1 inf	3.62	986	0	118	613	109	22.1	1.9	11.3
	RAPS 1 eff	6.97	1073	104	4	375	137	1.1	1.3	<0.5
	RAPS 2 inf	4.57	1185	5	203	801	119	37.1	4.4	23
	RAPS 2 eff	6.84	1354	171	15	571	204	3.4	4.7	<0.5
	Wetland eff	6.65	1180	83	48	529	161	11	3.6	3.9
03-Mar-04	RAPS 1 inf	3.9	1011	0	98	579	110	19.9	1.6	9.6
	RAPS 1 eff	7.64	1101	108	4	349	142	1	1.3	<0.5
	RAPS 2 inf	5.15	1170	10	197	779	117	39	4.5	21.3
	RAPS 2 eff	7.3	1482	182	16	653	230	3.5	5.6	<0.5
	Wetland eff	6.61	1122	67	61	472	148	12.2	3.4	5.9

FUTURE PLANS

Finalising planting and optimising hydraulic behaviour

As has already been mentioned, the Bowden Close system is not yet fully commissioned. When the overflow on RAPS 2 has been eliminated, so that all of the water passes through the reactive substrate, and when the aerobic wetland has been fully planted up and experienced one or two seasons of growth, we expect to polish the remaining 10 mg/l Fe in the final effluent to less than 2 mg/l (cf Batty and Younger 2002).

Research initiatives: TDP5, CoSTaR, ASURE and ESLs

The Bowden Close system benefits from substantial research support. Its status as CL:AIRE TDP5 has already been mentioned; besides providing a pathway to significant research funding from BOC Foundation and some of CL:AIRE's own sponsors, this link is crucial to the dissemination of research findings. A full TDP report is planned to be produced in due course, as soon as an assessment of the performance of the system can be made following full commissioning. Also through the link with CL:AIRE, this system has been clustered with five others to form 'CoSTaR', an unique national facility for mine site remediation research. As well as making six highly-characterised full-scale systems available for UK research (which includes the current Bioremediation LINK project 'ASURE', involving both the University of Wales, Bangor, and Newcastle University), CoSTaR has recently been designated an "international access infrastructure" by the European Commission 6th Framework Programme. This means that researchers from all over Europe will be able to receive funding to spend significant periods of time at Bowden Close and the other CoSTaR sites, collecting data of their own and learning about passive mine water remediation in the process. Even more research infrastructure support is to be provided by the University of Newcastle through its approved spending of SRIF2 funding provided by HEFCE. As part of a wider initiative to create a network of outdoor research facilities (termed "Earth Systems Laboratories") across the north of England, the CoSTaR sites are scheduled to receive further infrastructure investment with a total value in excess of £400K. This will not only ensure that hydraulic structures and sampling facilities at all CoSTaR sites match those which are now being commissioned at Bowden Close, but will also facilitate real-time telemetric transmission of flow and chemistry data back to the University campus, whence they will be further available to collaborating researchers world-wide via the web.

ACKNOWLEDGEMENTS

The Bowden Close Pilot System was funded under the Entrust Landfill Tax Credit Scheme by the County Durham Environmental Trust (CDENT) and managed by Neal McCay of Durham County Council. Balfour Beatty constructed the full-scale system on behalf of Durham County Council. Research and monitoring facilities in the full-scale system have been funded by the BOC Foundation and CL:AIRE. Susie Roy of Durham University kindly made data available for the Bowden No 3 discharge. Some of the work reported was part-funded by the European Commission FP5 R&D Project 'PIRAMID' (EVK1-CT-1999-000021; www.piramid.org), and also by the Biorem 4 LINK project 'ASURE' (co-funded by Rio Tinto, Scottish Coal, Parkhill Estates Ltd and IMC Ltd). Numerous staff and students have contributed to fieldwork over the years, most notably: Mr Patrick Orme, Dr Adam Jarvis, Dr Paula Canteli, James Coulson and Marian Diaz Goebes. The views expressed are the responsibility of the author alone and cannot be construed as representing the views of any of the sponsoring organisations.

REFERENCES

Amos P.W. and Younger P.L. 2003. Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate. *Water Research* **37**: 108 - 120.

Batty L.C. and Younger P.L. (2002) Critical role of macrophytes in achieving low iron concentrations in mine water treatment wetlands. *Environmental Science & Technology* **36**: 3997 - 4002.

Beck P., Harries N., and Sweeney R. 2001. *Design, installation and performance assessment of a zero valent iron perme-able reactive barrier in Monkstown, Northern Ireland*. CL:AIRE Technology Demonstration Report TDP3. (ISBN 0-9541673-0-9). CL:AIRE, London. 120pp.

Jarvis A.P. and Younger P.L. 1997. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK. *Chemistry and Ecology* **13**: 249 - 270.

Kepler D.A. and McCleary E.C. .1994. Successive Alkalinity Producing Systems (SAPS) for the Treatment of Acidic Mine Drainage. *Proceedings of the International Land Reclamation and Mine Drainage Conference and the 3rd International Conference on the Abatement of Acidic Drainage.* (Pittsburgh, PA; April 1994). Volume 1: Mine Drainage: 195 - 204.

Kepler, D.A. and E.C. McCleary, 1997, Passive aluminum treatment successes. In *Proceedings of the 18th Annual West Virginia Task Force Symposium*, held Morgantown, West Virginia, 15 - 16 April 1997.

Taylor L.T. and Jones D.M. 2001. Bioremediation of coal tar PAH in soils using biodiesel. *Chemosphere* **44**: 1131-1136.

Watzlaf G.R., Schroeder K.T., and Kairies C. 2000. Long-term performance of alkalinity-producing passive systems for the treatment of mine drainage. *Proceedings of the 2000 National Meeting of the American Society for Surface Mining and Reclamation*, Tampa, Florida, June 11-15, 2000.

Younger P.L. 1995. Hydrogeochemistry of minewaters flowing from abandoned coal workings in the Durham coalfield. *Quarterly Journal of Engineering Geology* **28**: S101 - S113.

Younger P.L. 2000. *Pilot-scale passive treatment of acidic mine drainage using a downward-flow,reducing and alkalinity producing system (RAPS) at Bowden Close, County Durham, UK.* Final report to Durham County Council and CDENT. University of Newcastle Upon Tyne, UK. 18pp.

Younger, P.L. 2002. A reducing and alkalinity-producing system (RAPS) for the passive treatment of acidic, aluminium-rich leachates emanating from revegetated colliery spoil materials at Bowden Close, County Durham. In Proceedings of the CL:AIRE Annual Project Conference, 11th April 2002, Imperial College, London. (ISBN 0-9541673-1-7). Paper 7, 21pp.

Younger P.L., Banwart S.A., and Hedin R.S. 2002. *Mine Water: Hydrology, Pollution, Remediation.* Kluwer Academic Publishers, Dordrecht. (ISBN 1-4020-0137-1). 464pp.

Younger, P.L., Jayaweera, A., Elliot, A., Wood, R., Amos, P. Daugherty, A.J., Martin, A., Bowden, L., Aplin, A.C., and Johnson, D.B. 2003. Passive treatment of acidic mine waters in subsurface-flow systems: exploring RAPS and permeable reactive barriers. *Land Contamination and Reclamation* **11**: 127 - 135.

Biographical Note

Professor Robert Kalin

Professor Robert Kalin is Professor in Environmental Engineering at Queens University Belfast and Director of the Environmental Engineering Research Centre. Current research concerns contaminated land remediation, groundwater geochemistry, and on the use of stable isotopes to indicate contaminant degradation. In the past 7 years, research grants at QUB in the areas of hydrogeology, groundwater geochemistry, biogeochemistry, and contaminated land total over £6 million. Two current EPSRC grants are related to treatment of contaminated land and groundwater, alongside an EPSRC Platform Grant for strategic support contaminated land and groundwater remediation research. There is ongoing international research on the use of isotope geochemistry for the understanding of groundwater flow dynamics and contaminant transport in both groundwater and surface water and are currently involved in the EU funded CORONA project for confidence in forecasting of natural attenuation.

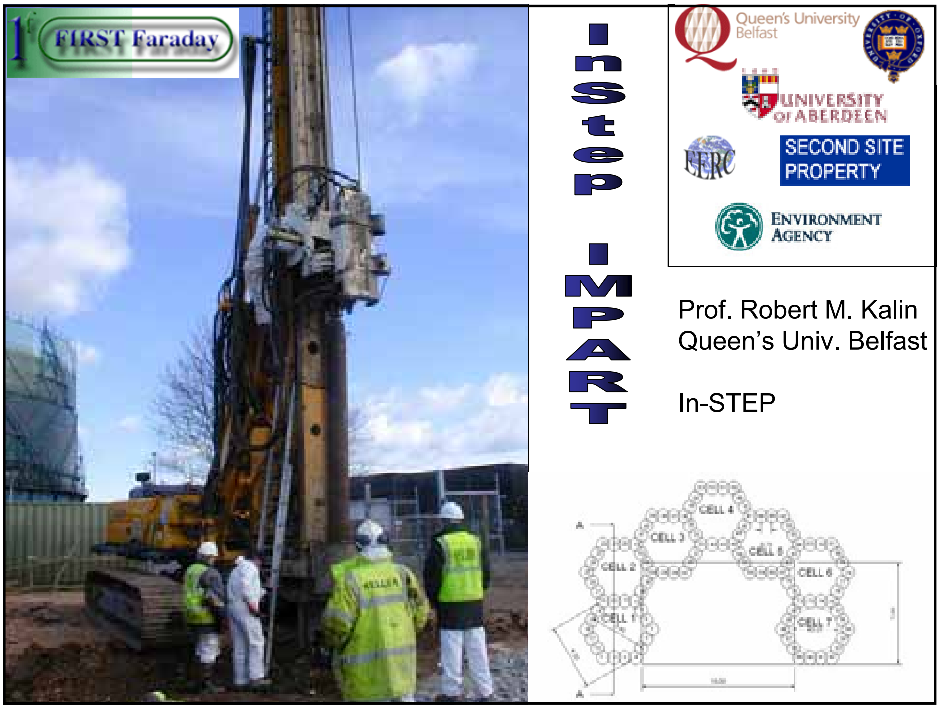
Dr Ian Thompson

Dr Ian Thompson leads the Microbial Diversity in the NERC Centre for Ecology & Hydrology, formerly the Institute of Virology & Environmental Microbiology. He was previously a Shell Fellow, at the University of Kent in collaboration with Shell Research and prior to that at the School of Environmental Sciences, University of East Anglia. He is co-founding member of the Oxford Centre for Environmental Biotechnology and the FIRST Faraday Partnership for Remediation.

His main research interest is focused on the diversity and activity of microbial populations that interact with organic pollutants, both in the environment and bioreactors. He has published over 80 papers and currently leads a research group consisting of 6 postdoctoral staff and 8 students, with a current research income of >£0.80m. Current research projects include biostimulating microbial degradation of pollutants in soil, phytoremediation of metals and organics, the application of electrokinetics (AC and DC) to manipulate microbial cells and contaminant availability, degradation of pesticides in groundwater and development of microbial systems for disposal of chemically mixed industrial wastes such as metal working fluids.

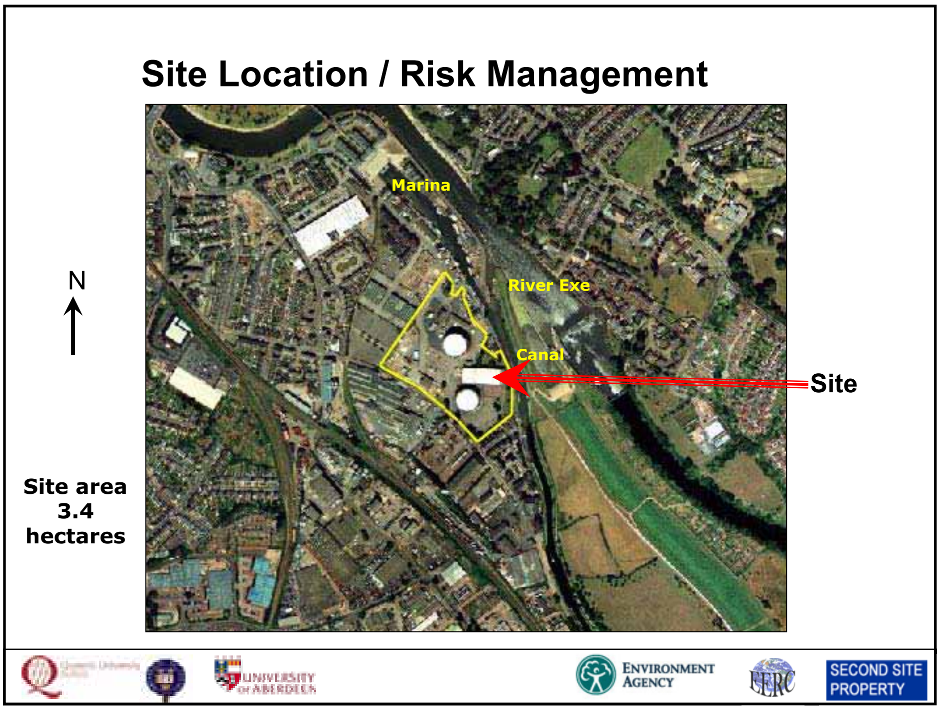
In situ source treatment for enhanced bioremediation processes

Robert Kalin



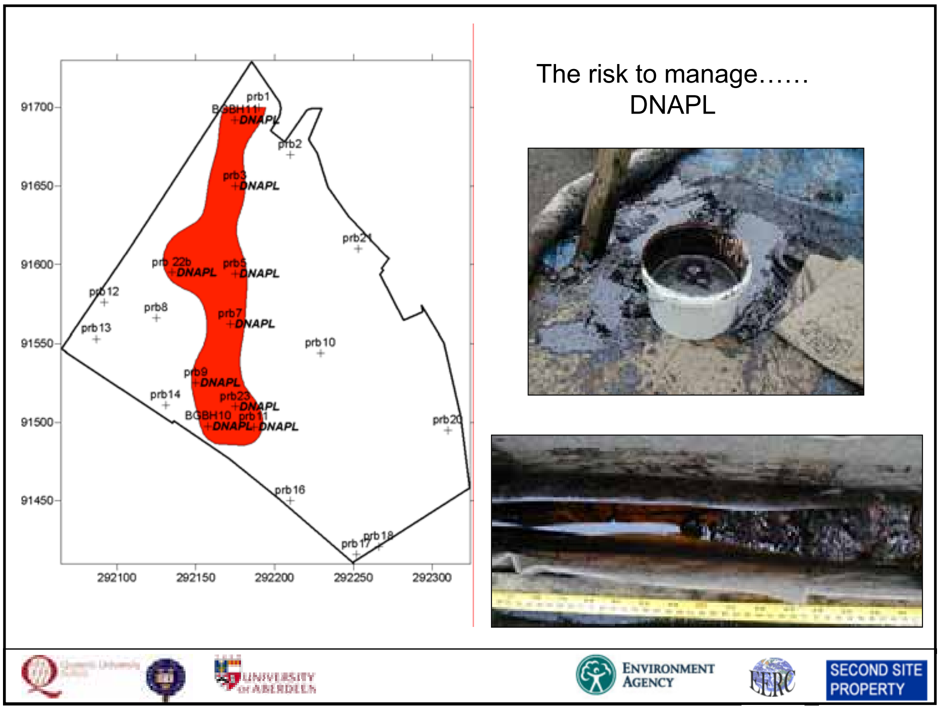
Prof. Robert M. Kalin
Queen's Univ. Belfast

In-STEP

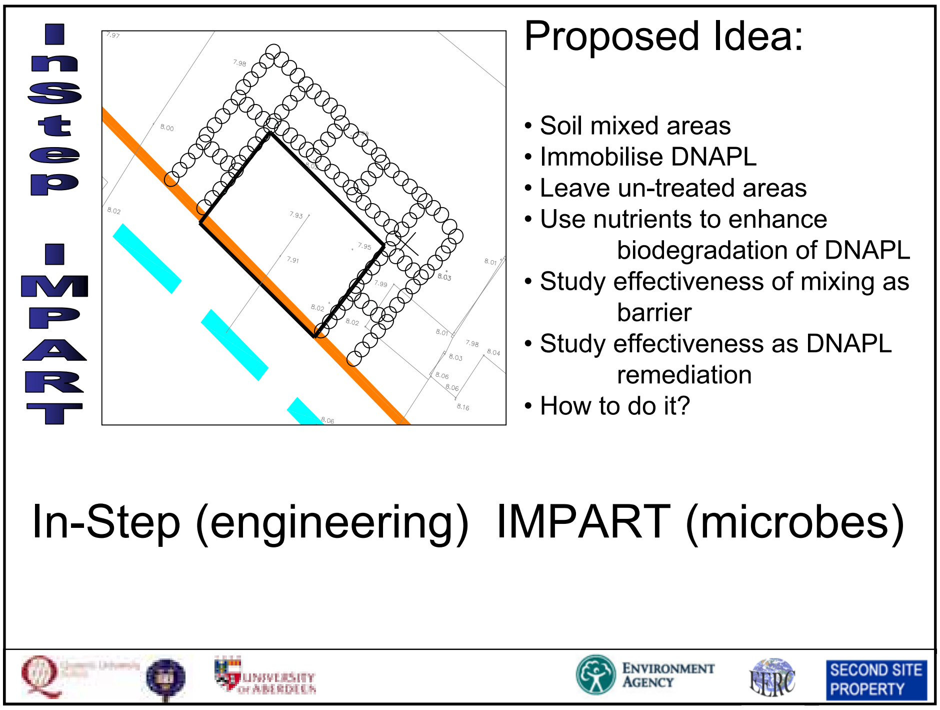


Site Location / Risk Management

Site area 3.4 hectares



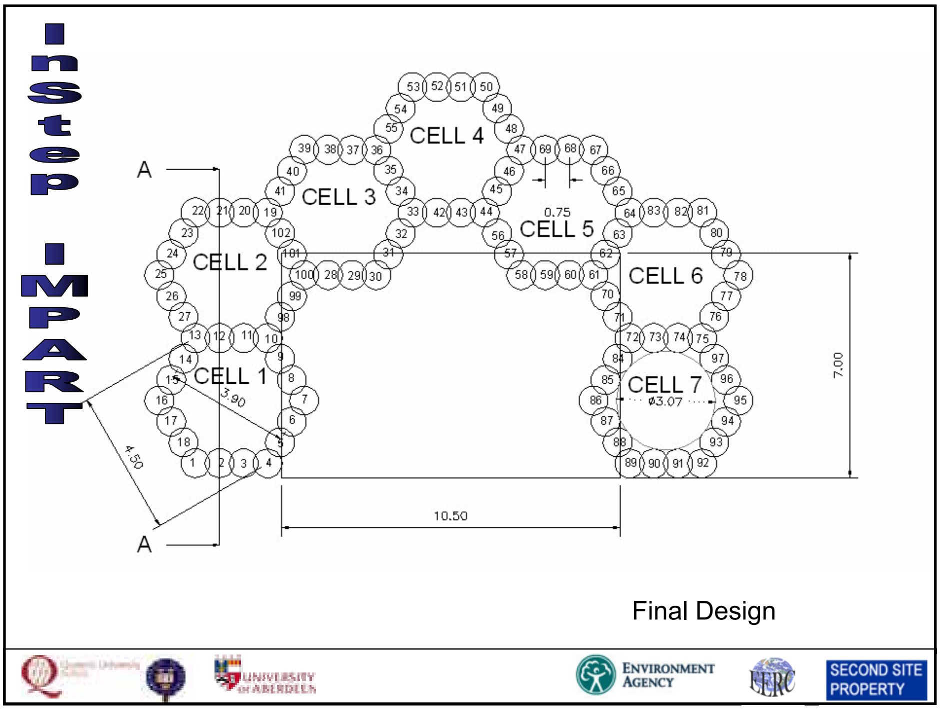
The risk to manage……
DNAPL



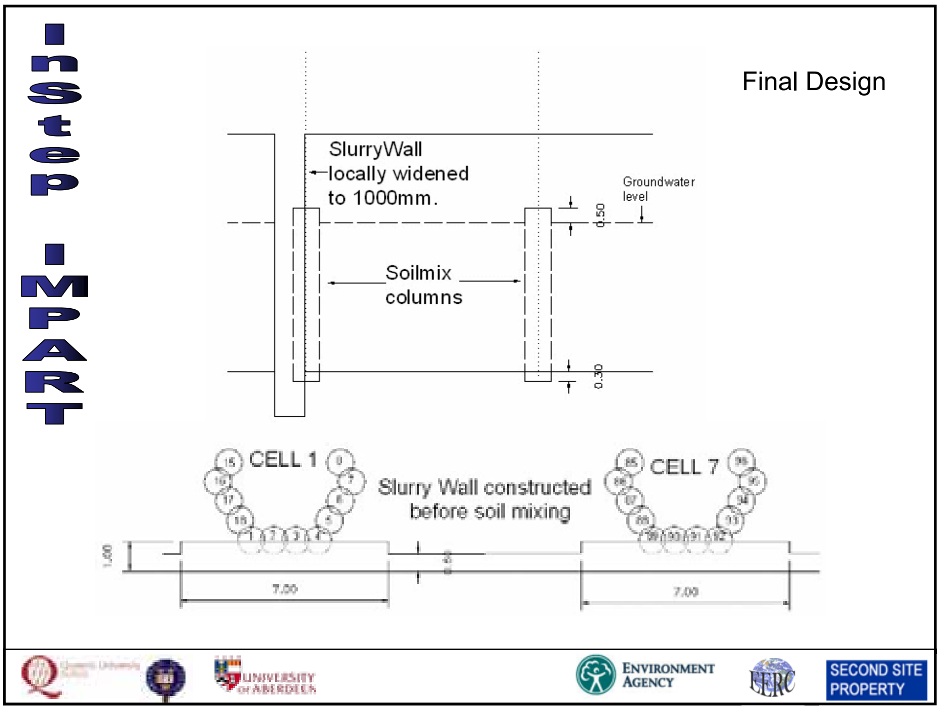
Proposed Idea:

- Soil mixed areas
- Immobilise DNAPL
- Leave un-treated areas
- Use nutrients to enhance biodegradation of DNAPL
- Study effectiveness of mixing as barrier
- Study effectiveness as DNAPL remediation
- How to do it?

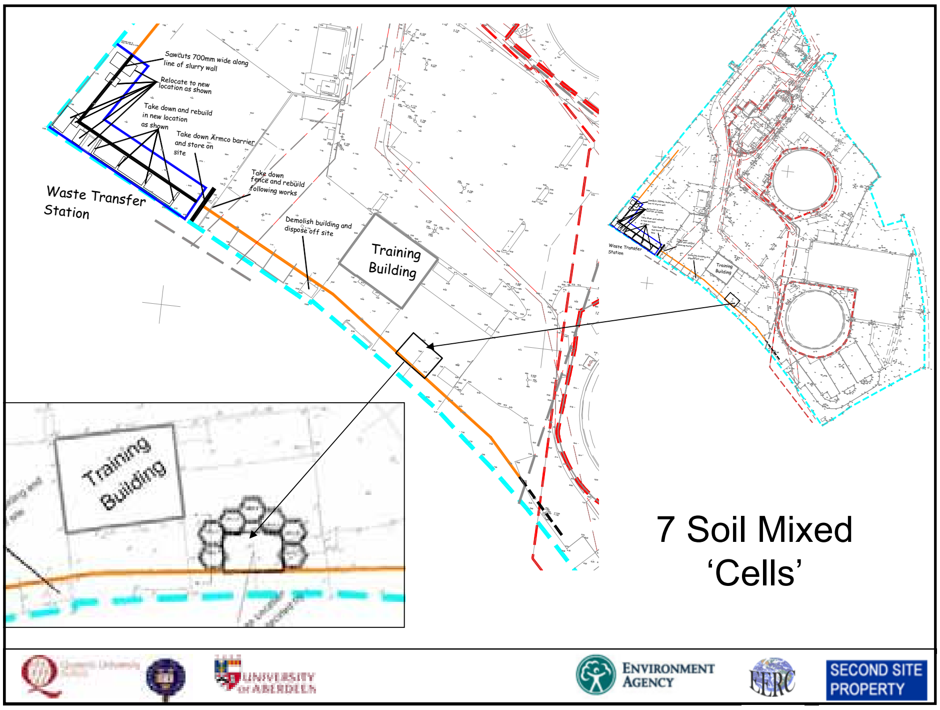
In-Step (engineering) IMPART (microbes)



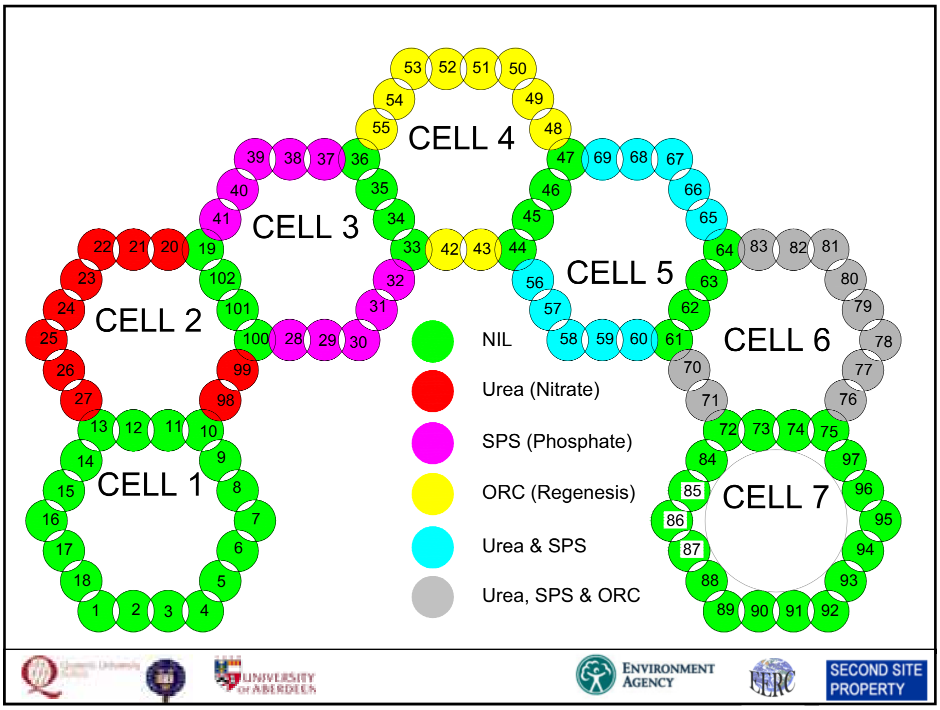
Final Design



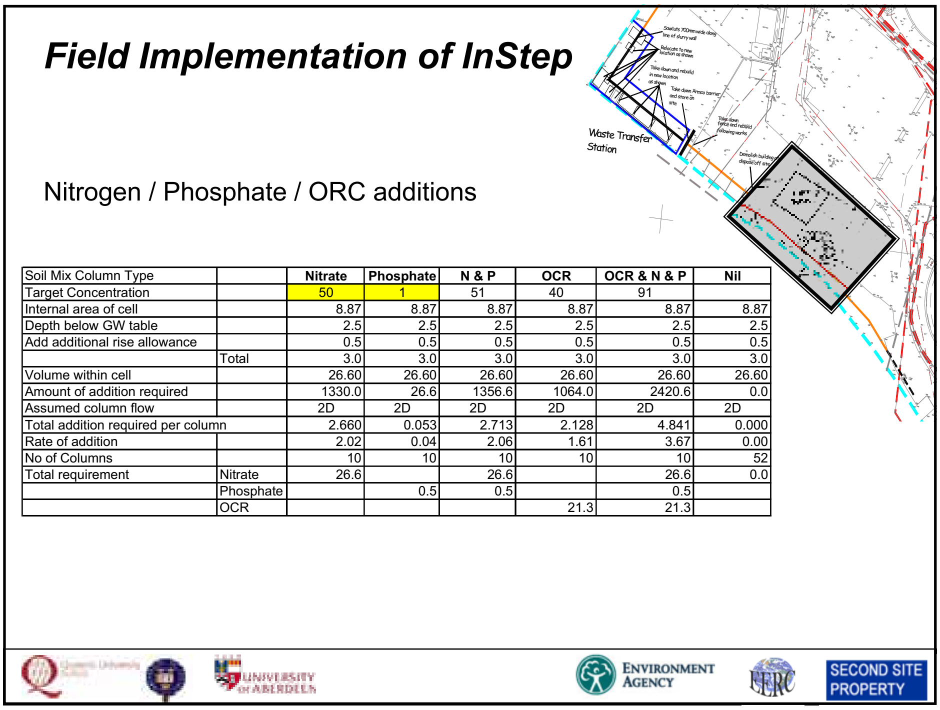
Final Design



7 Soil Mixed 'Cells'



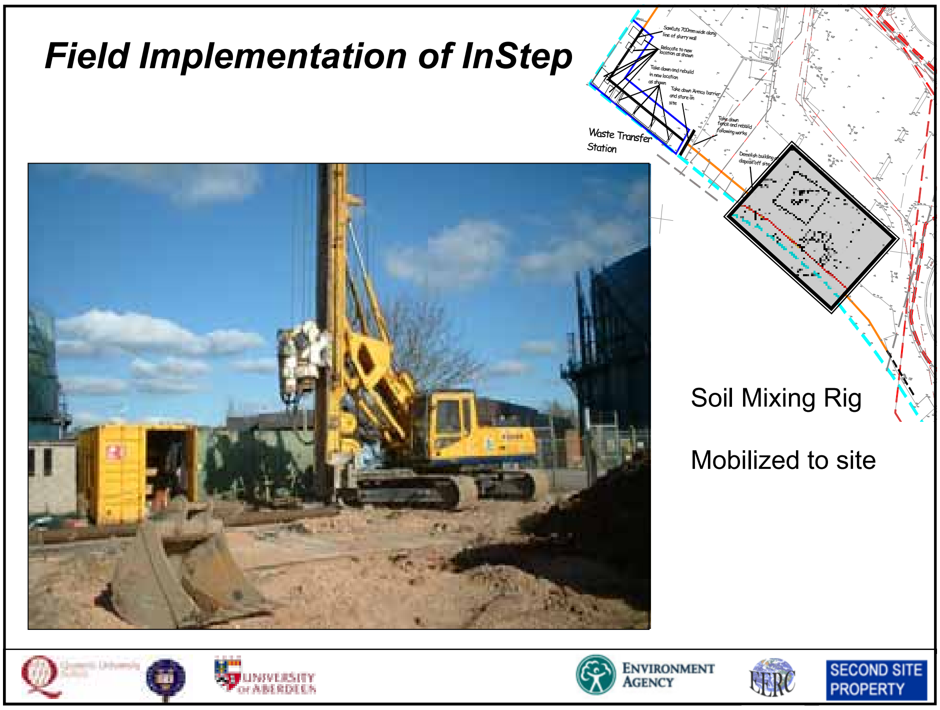
🟢 NIL
🔴 Urea (Nitrate)
🟣 SPS (Phosphate)
🟡 ORC (Regenesis)
🔵 Urea & SPS
⚪ Urea, SPS & ORC



Field Implementation of InStep

Nitrogen / Phosphate / ORC additions

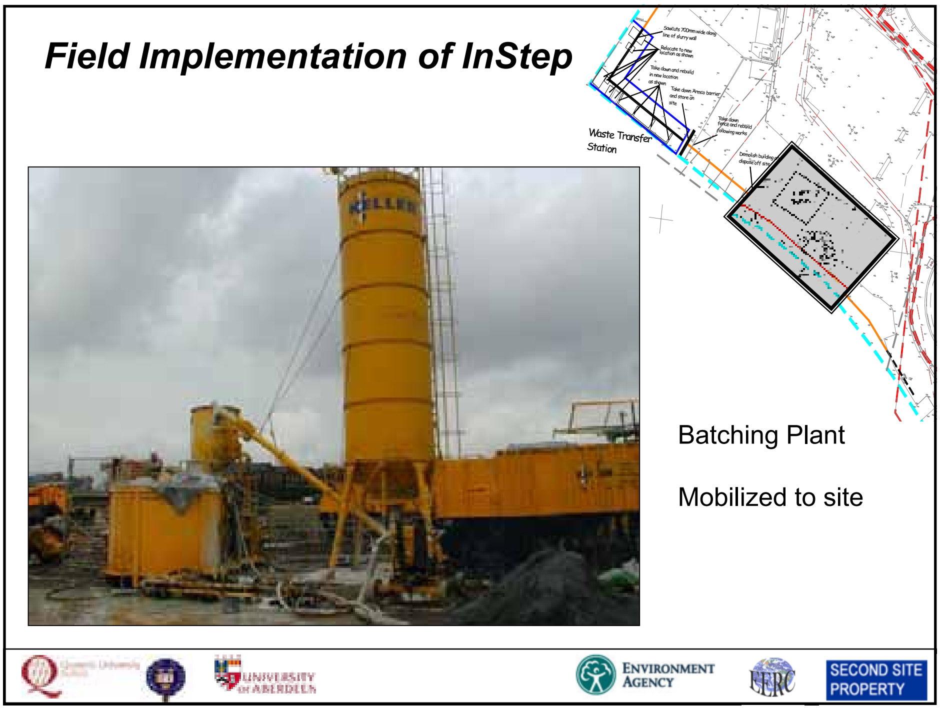
Soil Mix Column Type		**Nitrate**	**Phosphate**	**N & P**	**OCR**	**OCR & N & P**	**Nil**
Target Concentration		50	1	51	40	91	
Internal area of cell		8.87	8.87	8.87	8.87	8.87	8.87
Depth below GW table		2.5	2.5	2.5	2.5	2.5	2.5
Add additional rise allowance		0.5	0.5	0.5	0.5	0.5	0.5
	Total	3.0	3.0	3.0	3.0	3.0	3.0
Volume within cell		26.60	26.60	26.60	26.60	26.60	26.60
Amount of addition required		1330.0	26.6	1356.6	1064.0	2420.6	0.0
Assumed column flow		2D	2D	2D	2D	2D	2D
Total addition required per column		2.660	0.053	2.713	2.128	4.841	0.000
Rate of addition		2.02	0.04	2.06	1.61	3.67	0.00
No of Columns		10	10	10	10	10	52
Total requirement	Nitrate	26.6		26.6		26.6	0.0
	Phosphate		0.5	0.5		0.5	
	OCR				21.3	21.3	



Field Implementation of InStep

Soil Mixing Rig

Mobilized to site



Field Implementation of InStep

Batching Plant

Mobilized to site

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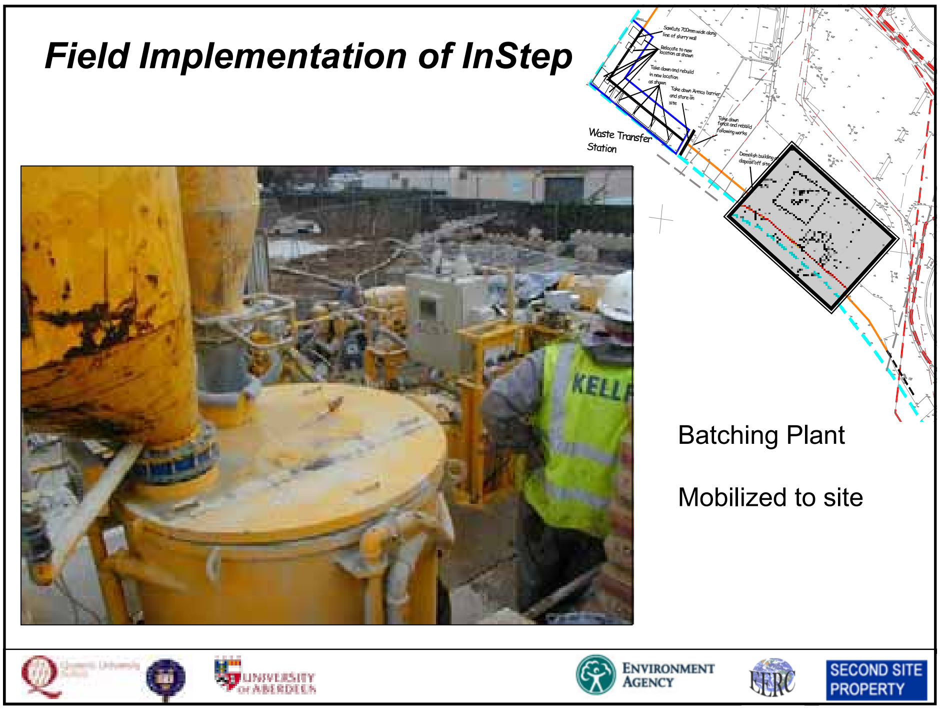
ENVIRONMENT AGENCY

SECOND SITE PROPERTY



Field Implementation of InStep

Batching Plant

Mobilized to site

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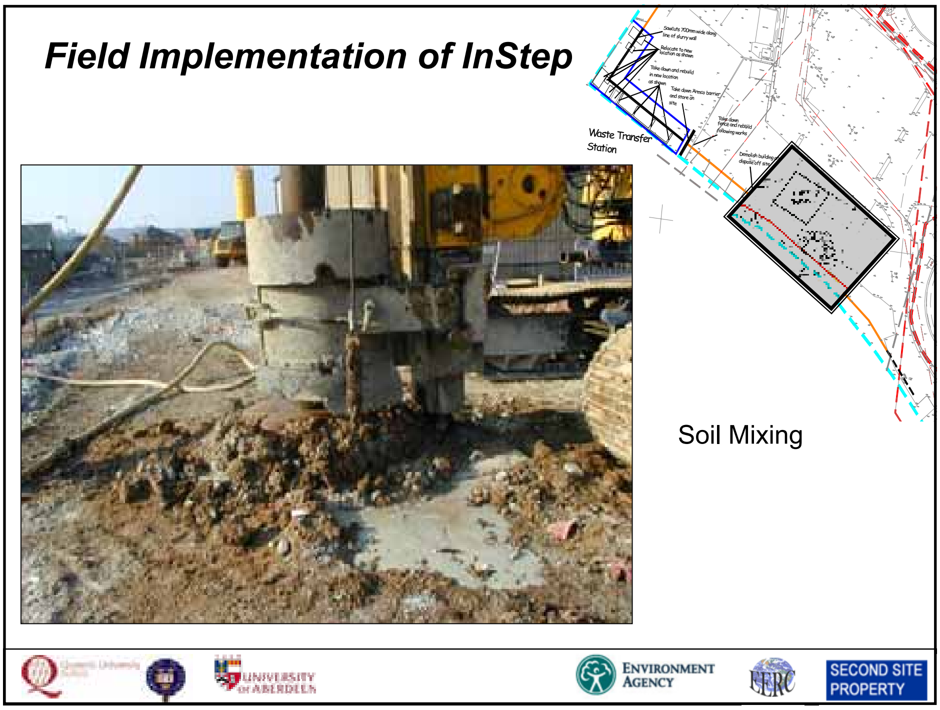
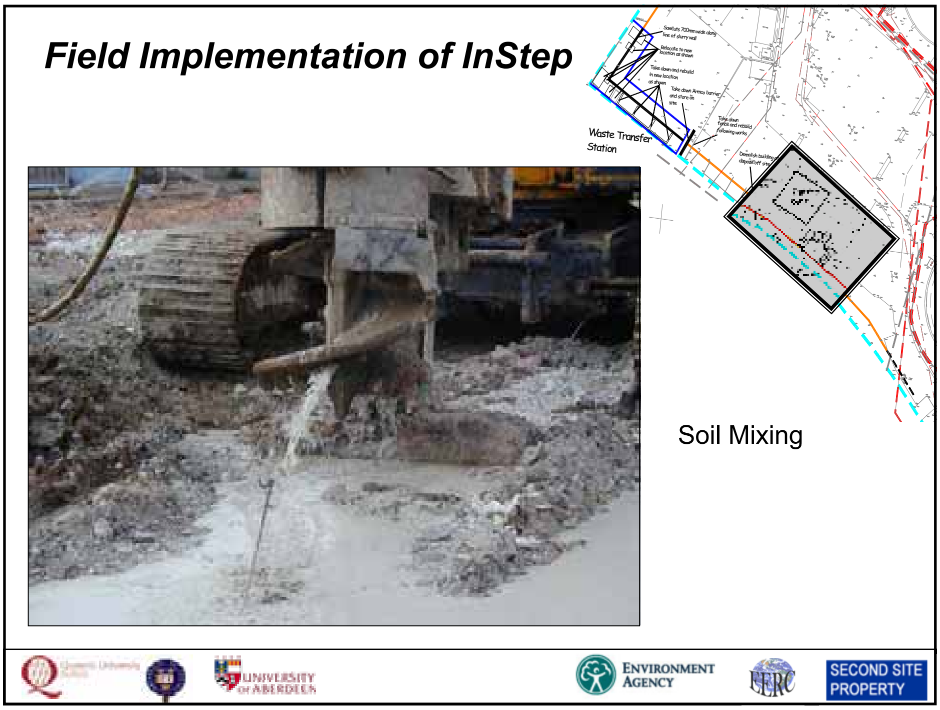
ENVIRONMENT AGENCY

SECOND SITE PROPERTY



Field Implementation of InStep

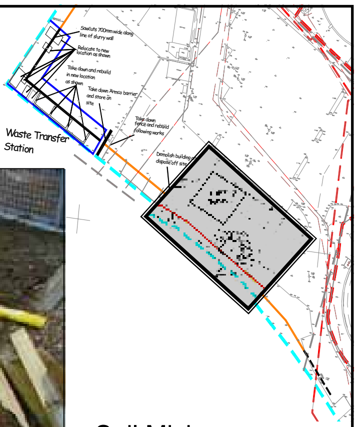
Soil Mixing



Field Implementation of InStep

Soil Mixing

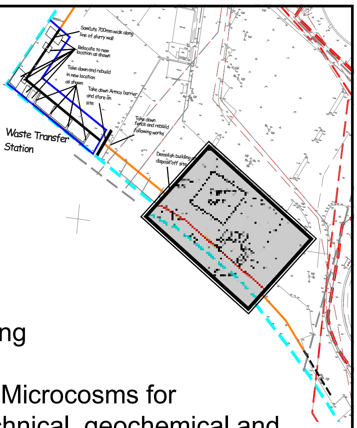
Field Implementation of InStep



Soil Mixing

DNAPL rising in
Soil mixed column

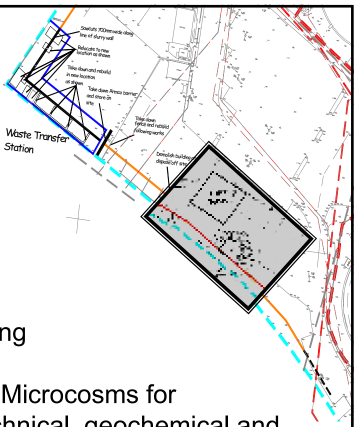
Field Implementation of InStep



Sampling

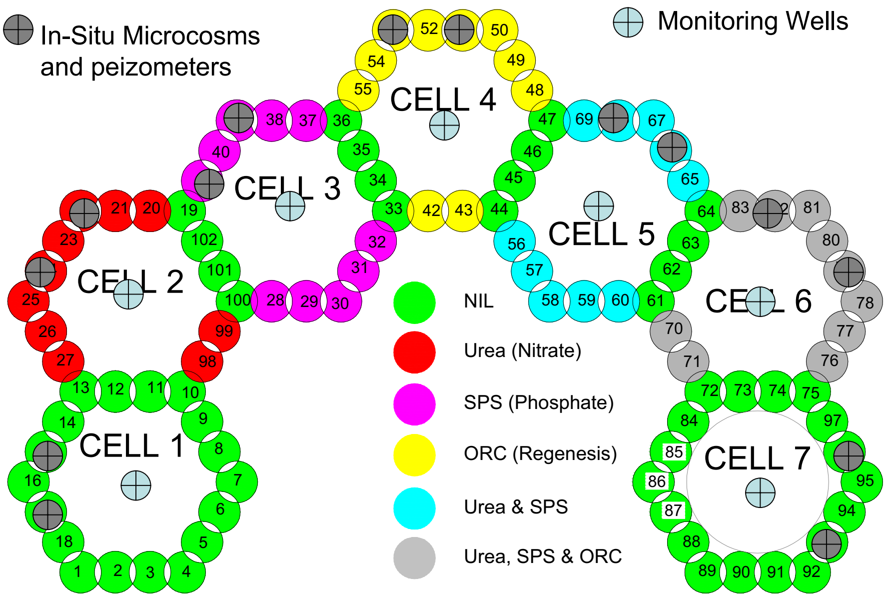
In-Situ Microcosms for
Geotechnical, geochemical and
Microbial study.

Field Implementation of InStep



Sampling

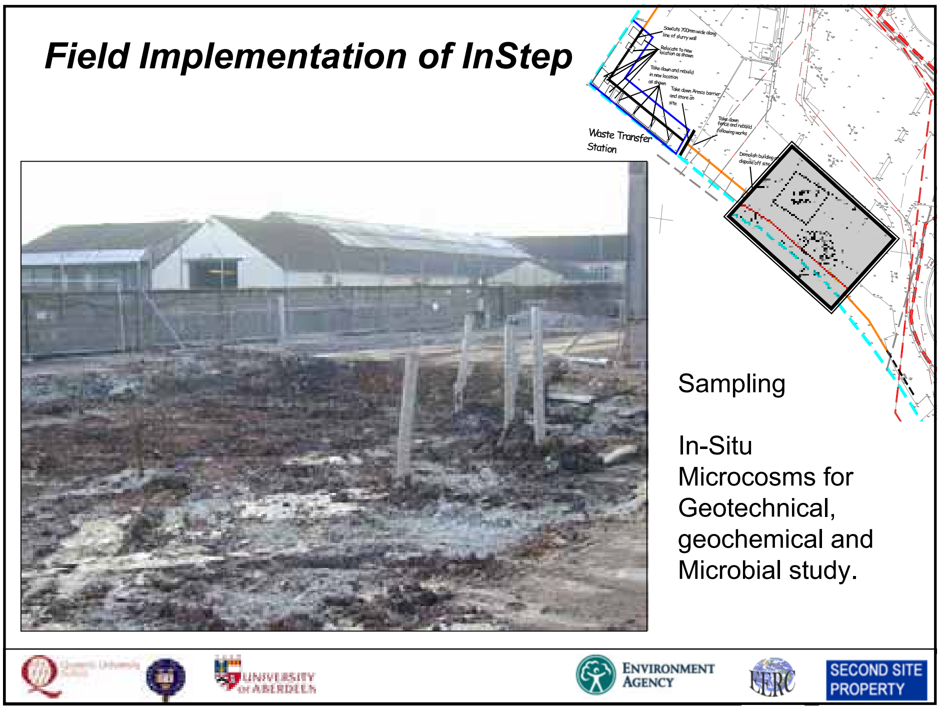
In-Situ Microcosms for Geotechnical, geochemical and Microbial study.



In-Situ Microcosms and peizometers

Monitoring Wells

- 🟩 NIL
- 🟥 Urea (Nitrate)
- ● SPS (Phosphate)
- 🟨 ORC (Regenesis)
- ● Urea & SPS
- ● Urea, SPS & ORC



Field Implementation of InStep

Sampling

In-Situ Microcosms for Geotechnical, geochemical and Microbial study.

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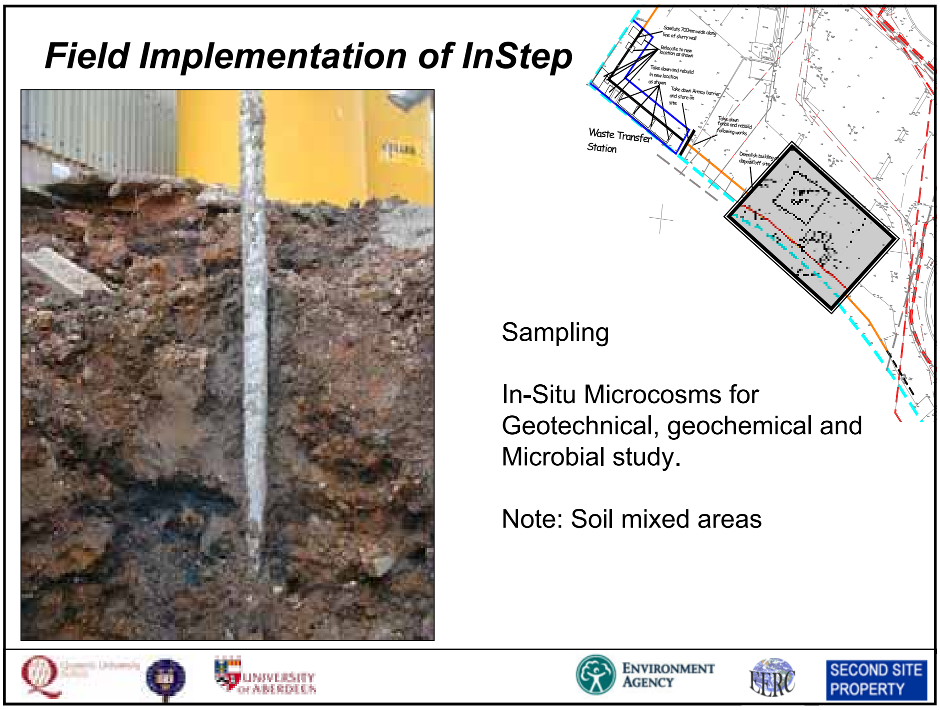
ENVIRONMENT AGENCY

SECOND SITE PROPERTY



Field Implementation of InStep

Sampling

In-Situ Microcosms for Geotechnical, geochemical and Microbial study.

Note: Soil mixed areas

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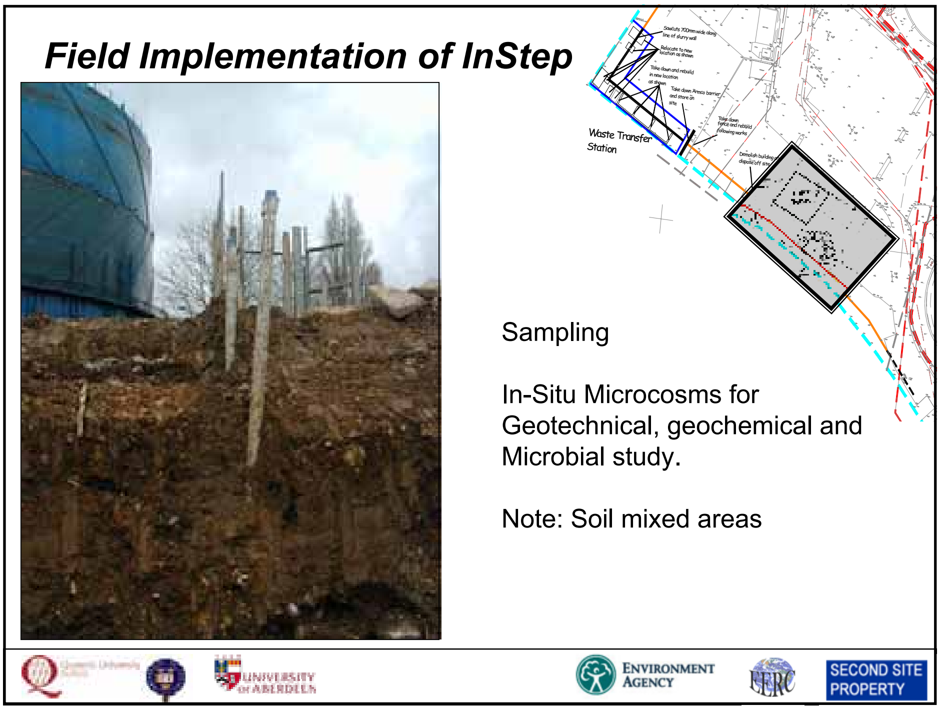
ENVIRONMENT AGENCY

SECOND SITE PROPERTY

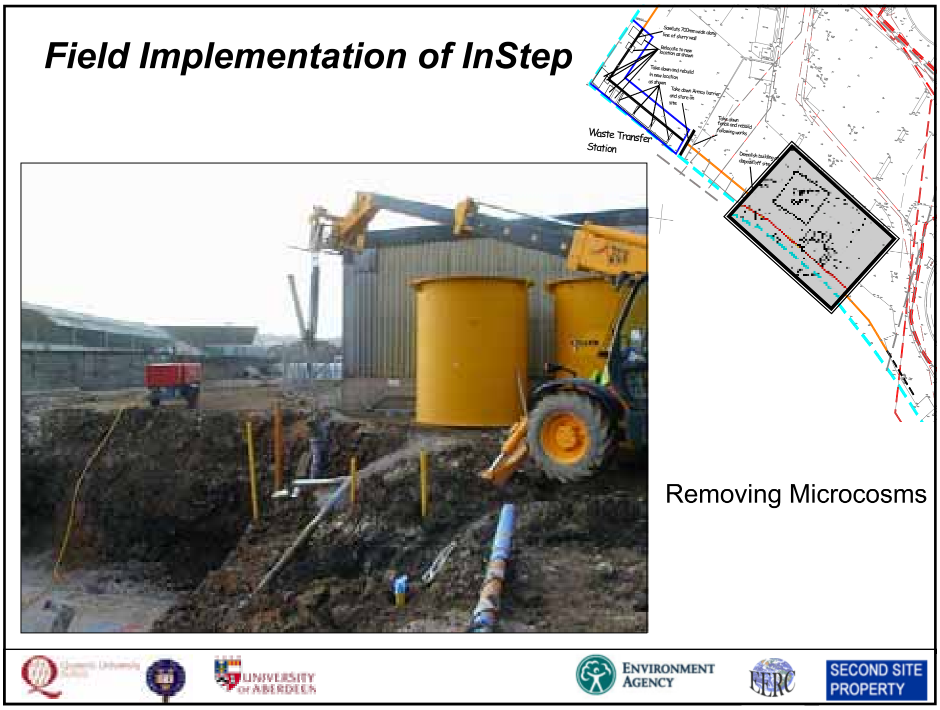


Field Implementation of InStep

Sampling

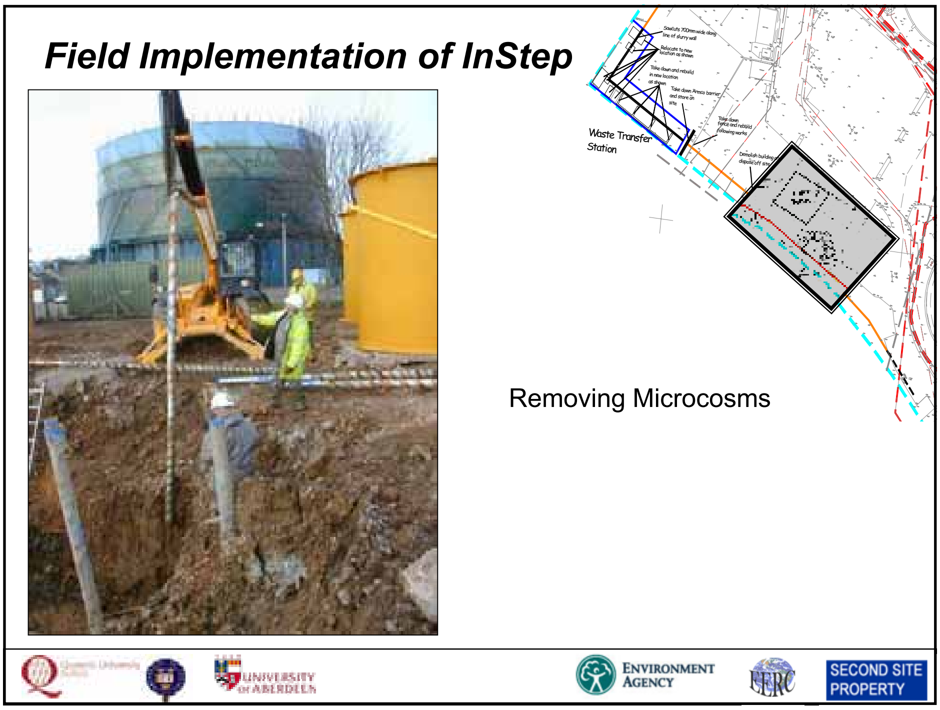
In-Situ Microcosms for Geotechnical, geochemical and Microbial study.

Note: Soil mixed areas



Field Implementation of InStep

Removing Microcosms



Field Implementation of InStep

Removing Microcosms

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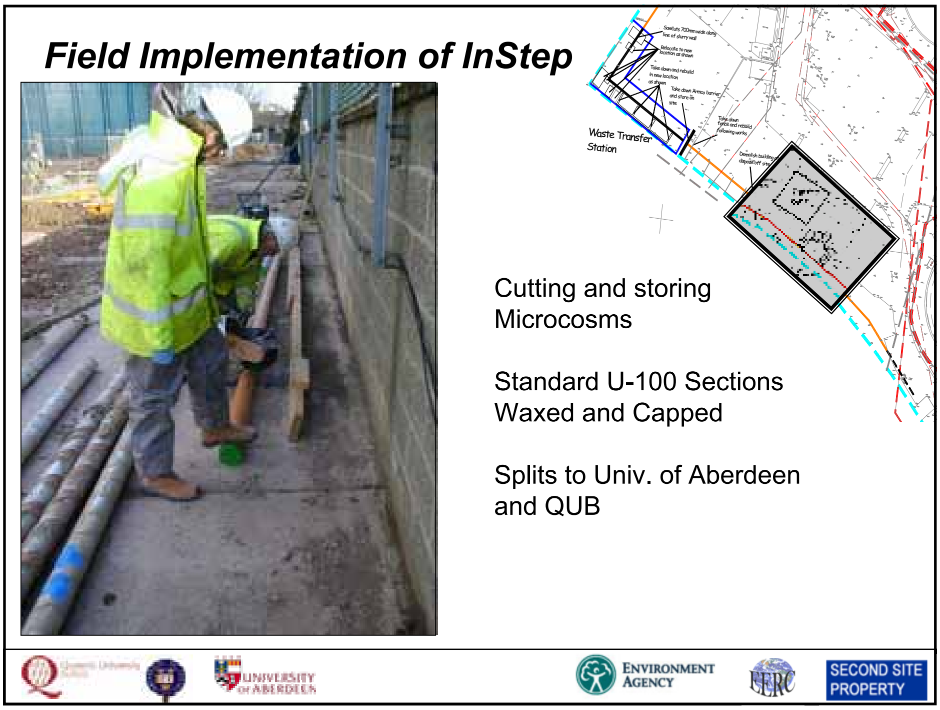
SECOND SITE PROPERTY



Field Implementation of InStep

Cutting and storing Microcosms

Standard U-100 Sections Waxed and Capped

Splits to Univ. of Aberdeen and QUB

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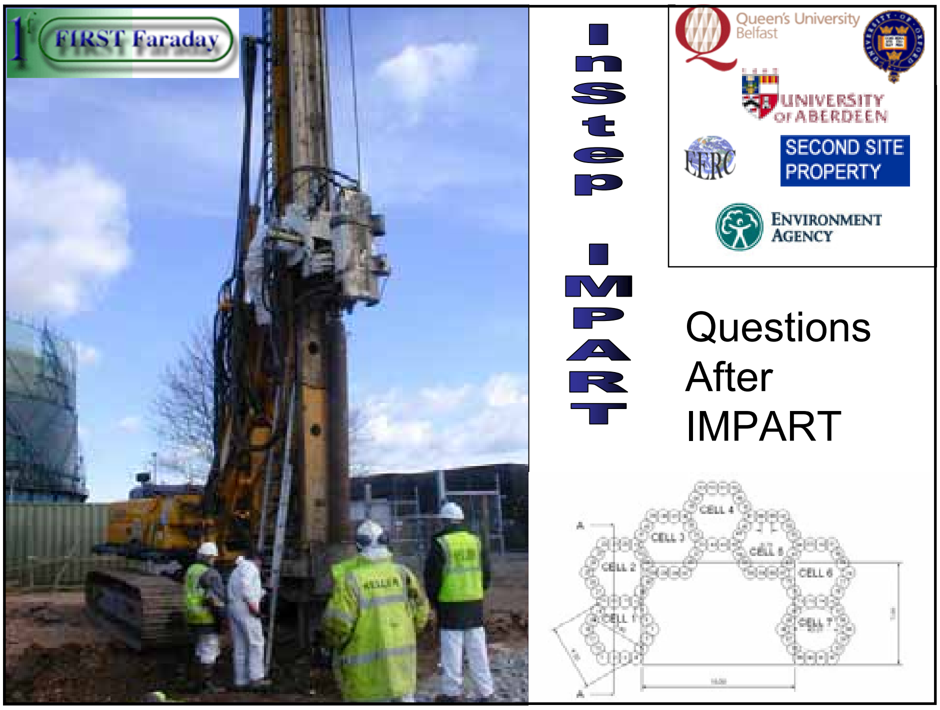
ENVIRONMENT AGENCY

SECOND SITE PROPERTY

In situ source treatment for enhanced bioremediation processes

Robert Kalin



InStep IMPART

Questions After IMPART

Microbial response to enhanced bioremediation processes

Collaborators

CEH Oxford
K. Ralebitso-Senior, I. Thompson

Queens University Belfast
K. Dickson, R. Kalin, M. Larkin, K. Lawson

University of Aberdeen
J. Dawson, K. Killham, G. Paton

Secondsite-Property
S. Wallace

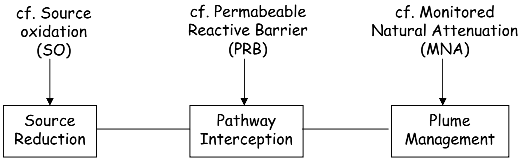
Rationale

Former town gas works sites in the North East UK, South West England & North East England (Only three of several hundred sites).

A range of contaminants, in both the saturated and unsaturated zones, incl. PAHs, BTEX, mineral oils and inorganics (cyanide & heavy metals).

Prime property in town/city centres.

In- & *Ex-situ* enhanced/engineered remediation ('Treament Train').



The 'Treatment Train'

Site contamination

An example of the extent of contamination on/near a former gas works site (North East England).

Enhanced/engineered remediation: Microbiology

Toxicity assays: Establish pollutant concentration and 'health' of indigenous catabolic microorganisms.

Chemical analyses: Measure concentration and bioavailability of existing contaminants.

Metabolic capacity: Establish existing degradative ability (catabolic species, genes & enzymes).

Community profiling (PCR-DGGE): Identify and understand occurring interacting microbial associations which degrade the contaminants; track community changes in response to different remediation technologies.

Enhanced/engineered remediation: Engineering

Understand site hydrogeology.

Contain, treat and manage contamination plume.

Circumvent decreased permeability and fouling inherent to most *in situ* biosupplementation/biostimulation treatments where delivery pipes are often blocked over time.

Effect a long-term sustained nutrient augmentation is with concomitant decrease in operational costs.

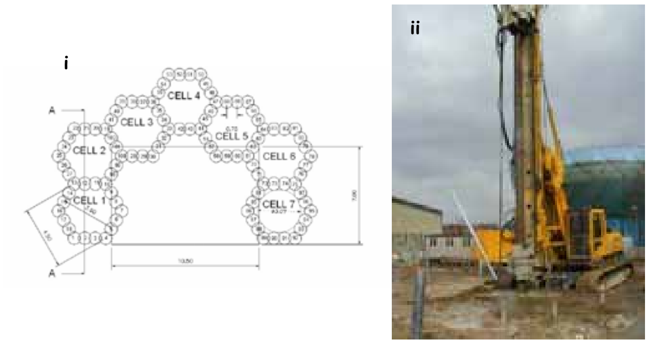
Identify key constraints to enhanced/engineered remediation.

Ex situ remediation

Soil homogenization and microcosm preparation in North East UK

Use approach to monitor *in situ* nutrient supplementation (South West England) and complement on site measurements.

In situ remediation



Schematic diagram of drilling, treatment cell preparation, pylon installation, *in situ* nutrient addition and sampling/monitoring in South West England (i). Picture of soil mixing rig at treatment cell 6 with U100 pipes before recovery for *ex situ* monitoring of soil columns in microcosms (ii).

Monitor *in situ* nutrient supplementation and use microcosms off site (North East UK) to complement on site measurements.

Treatments

Controls: pristine sites; contaminated soil without any treatment; pylons with no nutrients [M0].

Soil without any treatment, regular mixing to facilitate aeration; Reflect field management constraints [M1].

Mushroom compost (5% w/w): slow release of contaminants & reduce toxicity [M2].

Nutrient augmentation: nitrogen (N); phosphorus (P); oxygen (O, oxygen release compounds)[M3].

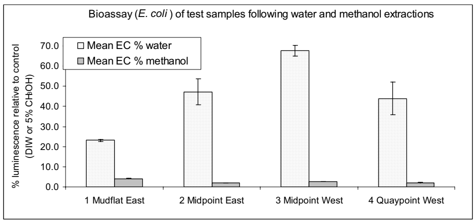
Surfactant: improve contaminant bioavailability [M4].

Secondary plant metabolites *e.g.* carvone, as biotransformation inducers.

Radio-labelled PAHs (naphthalene, phenanthrene or hexadecane); Monitor chemical fate; Detailed identification of functional populations.

Microcosms treatments in triplicate [a-c]: 20 kg fresh weight soil used to model *ex situ* remediation (North East UK) and monitor *in situ* treatments (South West England).

Analyses: Toxicity

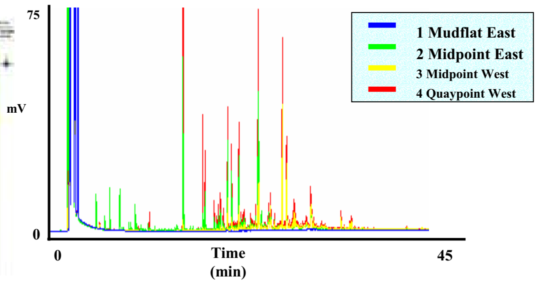


Biosensor analysis of North East England site sediments showed varying levels of toxicity with luminescence in water ranging between 20% and 70% of the control in an increasing order of Sediment 1>2>4>3.

Increased toxicity (<5% luminescence) was recorded for all sediments in 5% methanol.

High toxicity of the organic contaminants bound to the sediment matrix and not readily extractable by water but probably still bioavailable was, therefore, assumed.

Analyses: Chemical occurrence

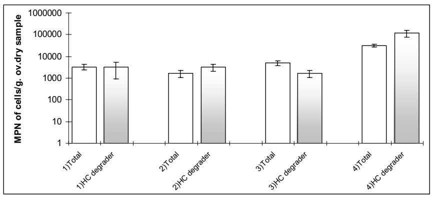


Sediment samples (1 - 4) showed a wide and diverse distribution of hydrocarbon contamination along the river shore with Sediment 4 showing generally the highest contamination by recalcitrant molecules and Sediment 2 characterized by lighter fractions.

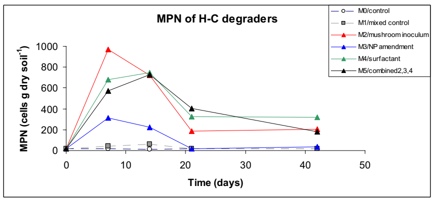
Contaminant concentration in Sediments: 1<2<3<4.

Site hydrogeology and distance relative to the source of contamination and tidal activity would account for the differences.

Analyses: Metabolic capacity

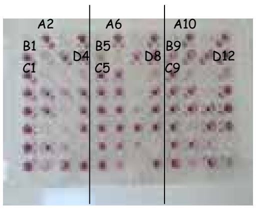


Most probable numbers (MPN) of total and hydrocarbon degrading microbial populations in a decreasing order of Sediment 3<1<2<4.

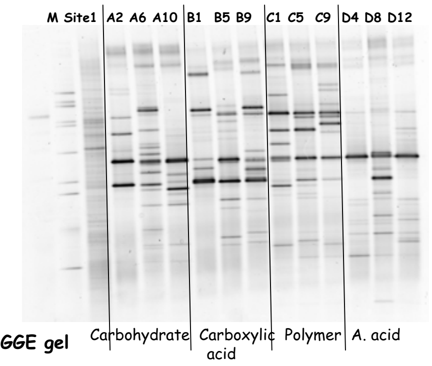


MPN of hydrocarbon (H-C) degraders in North East UK microcosms M0-M5 over 42 days of incubation

Analyses: Metabolic capacity



Biolog plate



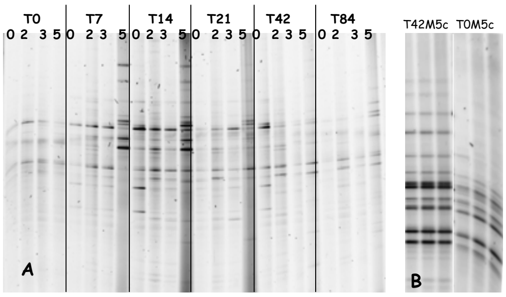
DGGE gel

Biolog plate: Substrate utilization patterns by a microbial community from a contaminated sediment.

DGGE gel: Explore the component species contributing to the physiological profiles.

Understand the metabolic capacities of indigenous species, individually and within the community.

Analyses: Community characterization



Key

M0: No treatment

M2: Mushroom

M3: N & P supplementation

M5: Mixed mushroom, nutrient & surfactant

16S rRNA gene separation on PCR-DGGE (40 – 60%) showing community profiles in microcosms M0, 2, 3 and 5 during the first 84 days of incubation (A). Profiles in microcosm 5c between 0 and 42 days (B)

Changes in microbial profiles between treatments and over time.

However, similarities in profiles suggest stable and robust microbial community on contaminated site independent of treatment.

Link community structure to chemical profile and, therefore, function and time.
Identify key profile(s): rapid indicator(s) for effective remediation.

Conclusions

Preliminary results of a 3 month investigation; early stages of a long-term study.

Current data serves as baseline and reflects the potential of enhanced/engineered remediation with circumvention of trial-and-error approaches.

Study reflects in-depth microbial characterisation of enhanced/engineered amelioration (new technology – 'treatment train' using cement encapsulation for nutrient delivery).

Understanding indigenous microbial systems and their response to the treatments/technology will facilitate the establishment of microbial robustness and accurate estimation of end-point and site recovery rates.

Site amelioration and monitoring will continue for a protracted period to consolidate and establish a long-term model for 60 (and up to 700) other former gas works sites.

Acknowledgements

- EPSRC
- NERC
- FIRST Faraday
- DTI

Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

Microbial response to enhanced bioremediation processes

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INTRODUCTION

Remediation of chemically-compromised sites has 3 general approaches: (i) source treatment; (i) interception or containment; and (iii) plume management. This study highlights a novel approach to the remediation of PAH-contaminated sites using a hybrid of both innovative and well-tested technologies. With the implementation of this 'treatment train', both the mass contaminant and treatment time should be markedly reduced. This is essential considering that, historically, gas works were located in town/city centres where the land is now increasingly valuable and efficient recovery is desirable. Therefore, in this study we test the hypothesis that a combination of soil mixing, for contaminant stabilisation, with nutrient addition can enhance natural attenuation in or near the source zone. In contrast to periodic nutrient injections, concrete encapsulation pylons saturated with nutrients will be adopted. The main benefit of the pylons is that they circumvent decreased permeability and fouling inherent to most *in situ* biosupplementation/biostimulation treatments where delivery pipes are often blocked over time (Stewart & Fogler 2002). Also, a long-term sustained nutrient augmentation is effected with a concomitant decrease in operational costs.

Since, site microbiology drives the bioremediation process, the need to understand its dynamics will be central to the investigations. Extensive attention will also be given to hydrogeology and geochemistry for a comprehensive 'bigger picture' site management.

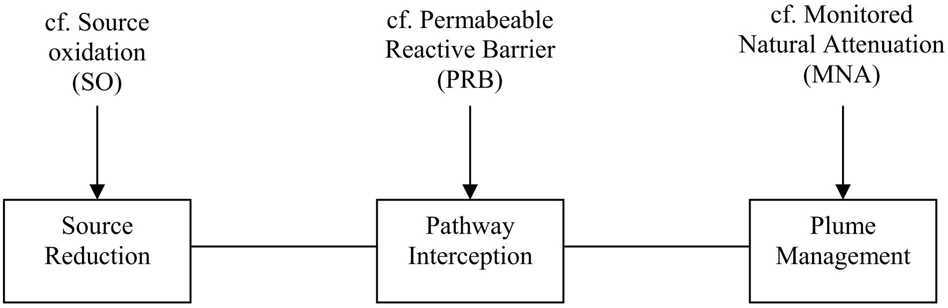


FIGURE 1: The treatment train

Overall objectives

Elucidate *in situ* enhanced/engineered remediation processes in former gas works sites. Simultaneously implement on- (*in situ*) and off- (*ex situ*) site supplementations with bioremediation enhancers *e.g.* nutrients.

METHODOLOGY

Sites

Three former gas works sites in North East UK, South West England and North East England, characterised by different soil types and hydrogeology profiles, were identified for the study. The contaminants, which occurred in the saturated and unsaturated zones, ranged from readily biodegradable BTEX and mineral oils and more recalcitrant PAHs and coal tars. A number of inorganic pollutants such as cyanide and heavy metals, characteristic of former town gas sites, were also present.

Contaminated soil was collected from the North East UK site and homogenised for *ex situ* treatments (Figure 2a) while concrete encapsulation pylons saturated with nutrients were installed in South West England (Figure 2b). The North East England site was investigated to explore contamination in different ecosystems/sites and therefore broaden our understanding of microbial responses under/to similar and diverse conditions/contaminants.

Treatments

These include:

(i) Controls of uncontaminated sites, contaminated soils with no nutrient/surfactant supplementation and concrete encapsulation pylons without nutrient addition [M0];
(ii) Contaminated soil without any treatment but mixed regularly to facilitate aeration and reflect field management constraints [M1];
(iii) Mushroom compost (5% w/w) addition to effect a slow release of contaminants and reduce toxicity [M2];
(iv) Nutrient augmentations with nitrogen (N); phosphorus (P); oxygen (O, oxygen release compounds) [M3];
(v) Surfactant (1% v/w) addition to facilitate contaminant bioavailability [M4]; and
(vi) Mixed mushroom, nutrient and surfactant supplementation [M5].

FIGURE 2a: Soil homogenization and microcosm preparation in North East UK

Sampling regime

The *in situ* biostimulation/biosupplementation treatments in South West England are monitored directly and in 20 kg soil microcosms together with the *ex situ* microcosms.

Sampling is made every week for the first 3 weeks and then every 6 weeks for the remainder of the studies, up to 302 days/10 months.

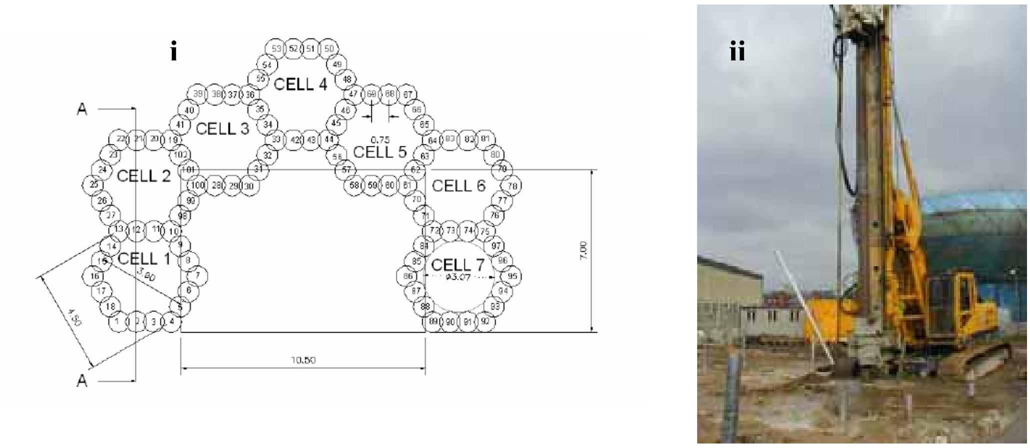


FIGURE 2b: Schematic diagram of drilling, treatment cell preparation, pylon installation, *in situ* nutrient addition and sampling/monitoring in South West England (i). Picture of soil mixing rig at treatment cell 6 with U100 pipes before recovery for *ex situ* monitoring of soil columns in microcosms (ii).

Analyses

To determine the effectiveness of the described remediation approach for stimulating biodegradation rates, it is essential to implement key analyses and these include:

(i) Chemical analysis with GC/HPLC to establish bioavailability and monitor contaminant degradation, and determine chemical fate using stable-isotope labelled contaminants (Manefield *et al*., 2002) in select microcosm treatment(s);

(ii) Toxicity assays to ascertain microbial response to the occurring contaminants and thus identify the need for complementary treatments, *e.g.* slow release of contaminants by the addition of mushroom compost, to facilitate/maintain microbial health for effective remediation; and

(iii) Molecular microbial ecology analyses to measure and monitor community profiles (PCR-DGGE), measure metabolic potential, probe for degradative genes and catabolic enzymes (microarrays/biochips) and identify key catabolic microbial associations using DNA-/RNA-based stable isotope probing (SIP) in specific microcosms.

RESULTS AND DISCUSSION

Current results reflect the early stages of a long-term investigation. They show preliminary data of a comprehensive protocol for subsequent *in situ* pollutant containment and treatment of three chemically-compromised gas works sites towards the development of a national code of practice.

The results of most probable number, respiration and Biolog analyses during the first 42 days of incubation showed differences between the *ex situ* microcosms depending on the treatment (Figure 3). In general, the different augmentations (mushroom, N+P, surfactant and combination) facilitated increased counts for the hydrocarbon degrading microorganims and, presumably, improved microbial health and metabolic/catabolic capacity.

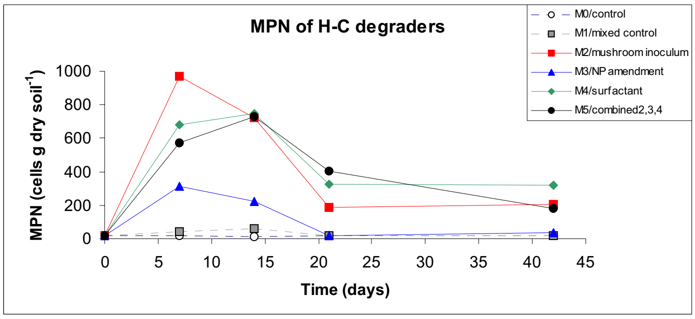


FIGURE 3: Most probable number of hydrocarbon (H-C) degraders in microcosms M0-M5 over 42 days of incubation

Molecular analysis complemented these findings with M5 (combined mushroom compost, N+P and surfactant supplementation) exhibiting an especially distinct profile (Figure 4a), probably in response to increased contaminant(s) bioavailability in the presence of the surfactant. This showed the resulting changes in metabolic (and catabolic) potentials and reflected the applicability of the approach/analyses for monitoring the performance of the remediation programmes.

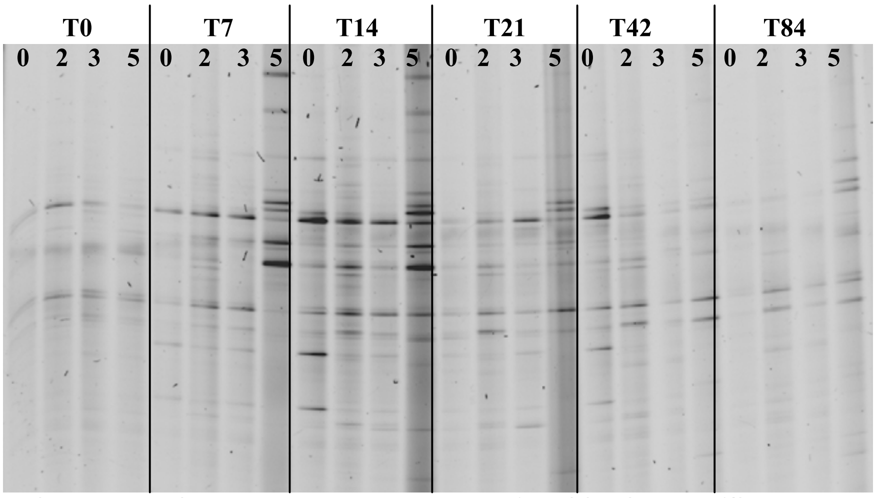


FIGURE 4a: 16S rRNA gene separation on PCR-DGGE (40 – 60%) showing community profiles in microcosms M0 (control), M2 (mushroom compost), M3 (N+P augmentation) and M5 (mixed mushroom, N+P and surfactant supplementation) during the first 84 days of incubation.

Reproducible profiles were visualized with PCR-DGGE within triplicate microcosms and indicated consistent treatments with 20 kg (fresh weight) of soil (Figure 4b). Thus the choice of an increased microcosm size never hitherto investigated was justified and the potential successes of *in situ* and large scale remediation programmes reflected fairly reliably.

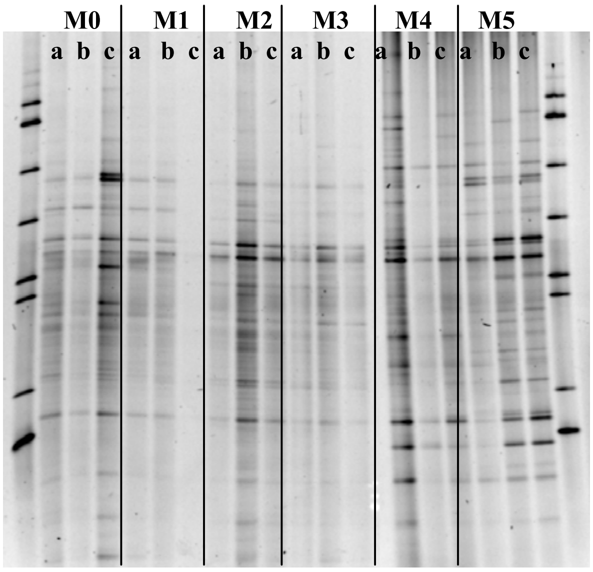


FIGURE 4b: 16S rRNA gene separation on PCR-DGGE (40 – 60%) showing community profiles in triplicate (a-c) microcosms M0 - M5 at day 84 of incubation.

Focus on one time point, T84 (Figure 4b), highlighted the similarities and differences of the occurring soil microbial communities and, thus, the effects of different enhanced remediations. In particular, the similarities suggested robust, indigenous populations.

A correlation of the metabolic potential changes and shifts in species profiles to chemical degradation will identify the key catabolic microbial members/communities and genes. Furthermore, confirmation of both the constant and changeable species, by techniques such as stable isotope probing, will establish the members that can be manipulated and exploited locally and nationally during different treatments in sites similarly contaminated with PAHs. The use of cutting edge technologies to link microbial community response to degradation has been demonstrated and proven to be an effective approach for exploiting such populations in contaminant clean-up (van der Gast *et al*., 2004). Therefore, along with DNA-/RNA-based SIP in soil microcosms, future work will include probing for PAH degradative genes, using microarrays/biochips, with particular focus on the *in situ* treatment of the chemically-compromised sites. This information will then be used in site remediation programmes to: (i) monitor treatment efficacy; (ii) identify the most effective treatment; (iii) predict time scales; and (iv) develop/establish some universal principles on chemically-compromised sites.

CONCLUSIONS

While general extrapolations may not be made from three sites after 3 months of investigations, the current data serves as a baseline and reflects the potential of enhanced/engineered remediation. With a decisive move from trial-and-error approaches, the current study reflects an in-depth microbial characterisation of enhanced/engineered amelioration and, later, the new technology of a ‘treatment train’ using cement encapsulation for nutrient delivery. By understanding the indigenous microbial systems and their response to the treatments/the technology, their robustness can be established while the end-point and site recovery rates can be accurately estimated. It is envisaged, therefore, that site amelioration and monitoring will continue for a protracted period to consolidate and establish a long-term model for 60 (and up to 700) other former gas works sites.

ACKNOWLEDGEMENTS

This work was funded by NERC, EPSRC, DTI and FIRSTFARADAY and implemented in collaboration with Secondsite-Property.

REFERENCES

Stewart, T.L. and Fogler, S.H. 2002. Pore-scale investigation of biomass development and propagation in porous media. *Biotechnol. Bioeng*., **77**, 577-588.

Manefield, M., Whiteley, A.S., Griffiths, R.I. and Bailey, M.J. 2002. RNA Stable Isotope Probing, a Novel Means of Linking Microbial Community Function to Phylogeny. *Appl. Environ. Microbiol.*, **68**, 5367–5373.

Van der Gast, C.J., Singer, A.S. and Thompson, I.P. 2004. Temporal dynamics and degradation activity of an bacterial inoculum for treating waste metal-working fluid. *Environ. Microbiol.,* **6**, 254-263.

Biographical Note

Professor Steve Banwart

Steve Banwart is Professor of Environmental Engineering Science and is a member of the Groundwater Protection and Restoration Research Group (GPRG) at the University of Sheffield. His main research activities are in Biodegradation Science, Soil and Groundwater Chemistry and Mine Water Pollution. He has a leading international track record in the study of reactive processes in soil and groundwater, having research work featured on the cover the journal Environmental Science and Technology and recently co-authoring a major new textbook on Mine Water Pollution. He received his PhD from the Swiss Federal Institute of Technology and was Research Faculty at the Royal Institute of Technology, Stockholm before moving to the UK in 1995 where he teamed up with David Lerner to establish the GPRG. He is Principle Investigator of the CL:AIRE project: Development of an In Situ Aquifer Assessment Tool funded by EPSRC as part of the FIRSTFARADAY Partnership on Remediation of Polluted Environments.

Dr Paul Nathanail

Paul Nathanail MA, MSc, PhD, CGeol, SILC is head of the Land Quality Management research group at the University of Nottingham and managing director of Land Quality Management Ltd - site characterisation and risk assessment specialists. His research interests span the entire spectrum of contaminated land characterisation, assessment and remediation as well as the sustainability aspects of urban regeneration.

FIRSTFARADAY

GPRG

Development of an In Situ Aquifer Assessment Tool

The Coalition Forces Attack Site Characterization Drawbacks

U. Sheffield
Steven Banwart
Mohamed Mohamed
Steven Thornton
Ryan Wilson
David Lerner
Alan Smalley
Duncan McKnight
Chris Berryman

U. Waterloo
Neil Thomson

U. Nottingham
Paul Nathanail
Matt Ashmore

Queens U. Belfast
Trevor Elliot

Shell Global Solutions

Environment Agency

CL:AIRE

BP

SecondSite

GPRG

Challenges for MNA Implementation

- Perception of a “non-technological” solution
  - Lack of process control
  - Possibility of long time frames for cleanup
- Low operating cost vs costly site model
- Design of site investigation becomes critical
  - Targeting the necessary data (transport, reactions, etc)
  - Obtaining representative data at minimal cost
  - Robust evaluation of uncertainty in performance

GPRG

Development of an In Situ Aquifer Assessment Tool (AAT)

Aims:

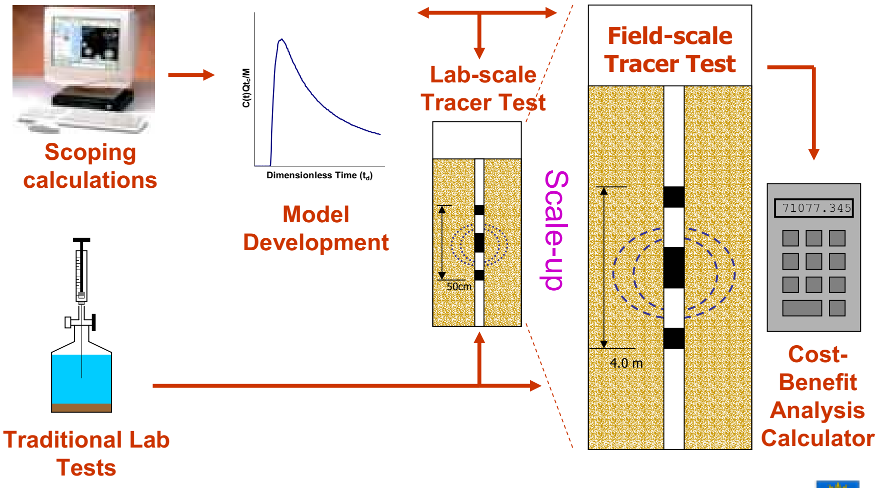
- Improve aquifer data collection related to natural attenuation
- Develop a borehole tracer test method to collect the data
- Test method in the field as "Proof-of-Concept"
- Develop Cost-Benefit-Analysis tool for Site Investigation

The Field Site

- Site for Innovative Research into Natural Attenuation (SIReN)

GPRG

Project Overview



Scoping calculations

Model Development

Lab-scale Tracer Test

Scale-up

Field-scale Tracer Test

Cost-Benefit Analysis Calculator

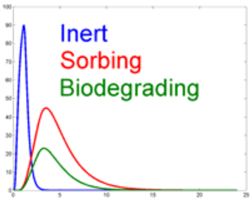
Traditional Lab Tests

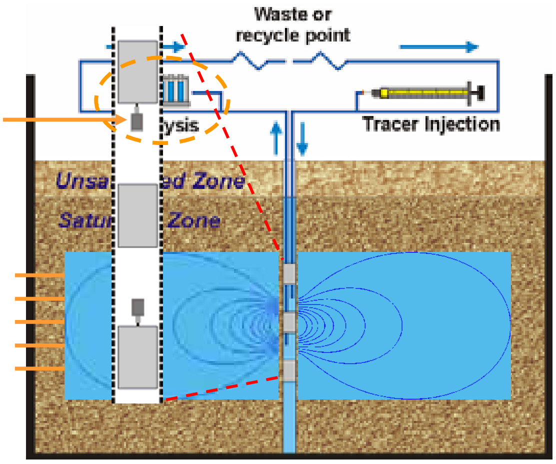
Deliverables

- Field and lab test results and supporting documentation
- Method for use of reactive tracers in site assessment
- Site Investigation CBA Calculator and guidance document
- Risk calculator for MNA implementation
- Evaluation of methodology for user needs
- Experimental platform for other *In Situ* science studies

How will the AAT work?

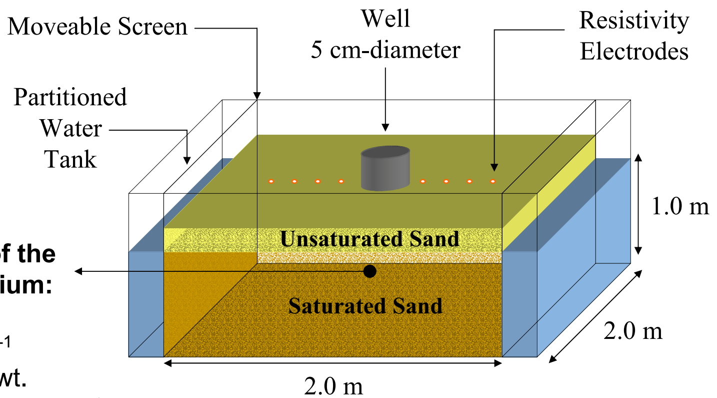
Tracer arrival at the extraction chamber is monitored and used to plot breakthrough curves (BTCs)





GPRG

The Sandbox Design

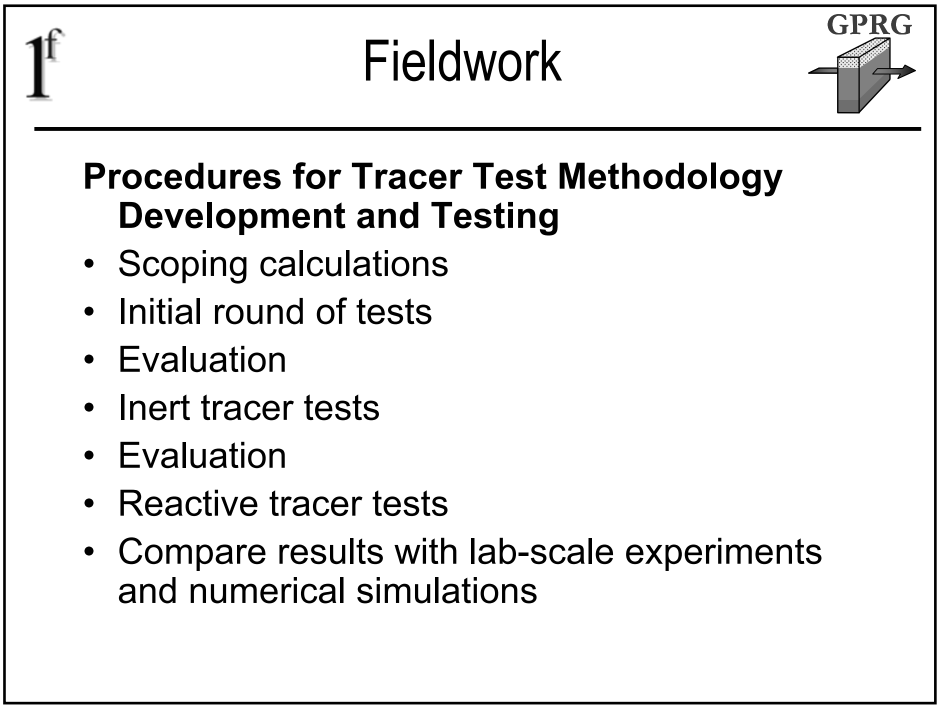


Properties of the porous medium:

- $k_r \approx 10^{-5}$ ms^{-1}
- $f_{OC} \approx 0.1\%$ wt.
- CEC > 1 meq $100g^{-1}$
- $CaCO_3 > 1$ % wt.
- Free & Active Fe > 1000 mg kg^{-1}
- Free & Active Mn > 10 mg kg^{-1}

GPRG

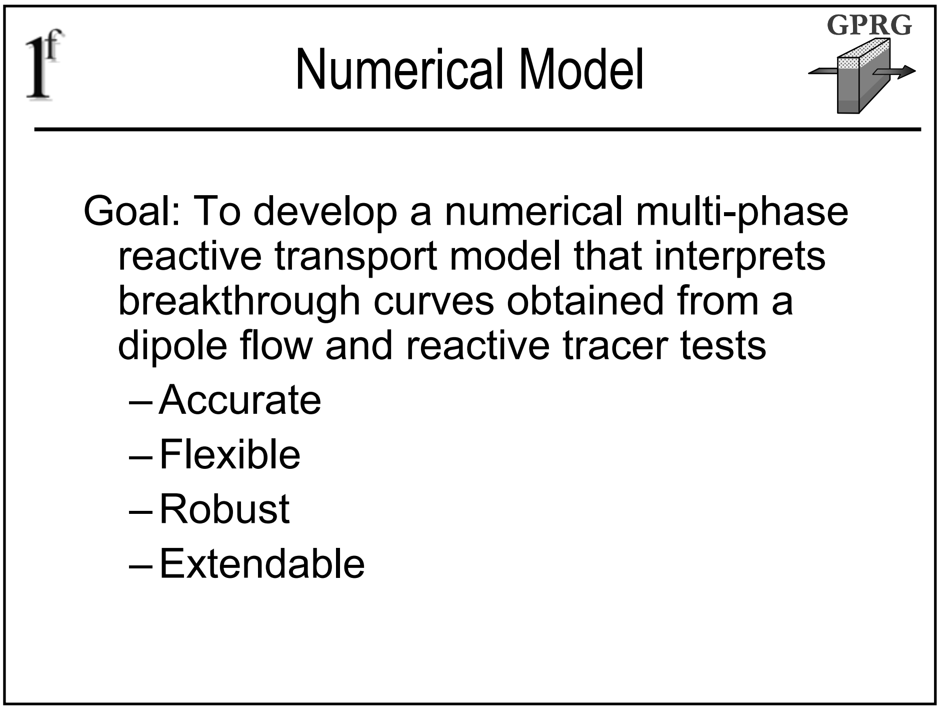
Sand Box for LabTests



Fieldwork

Procedures for Tracer Test Methodology Development and Testing

- Scoping calculations
- Initial round of tests
- Evaluation
- Inert tracer tests
- Evaluation
- Reactive tracer tests
- Compare results with lab-scale experiments and numerical simulations



Numerical Model

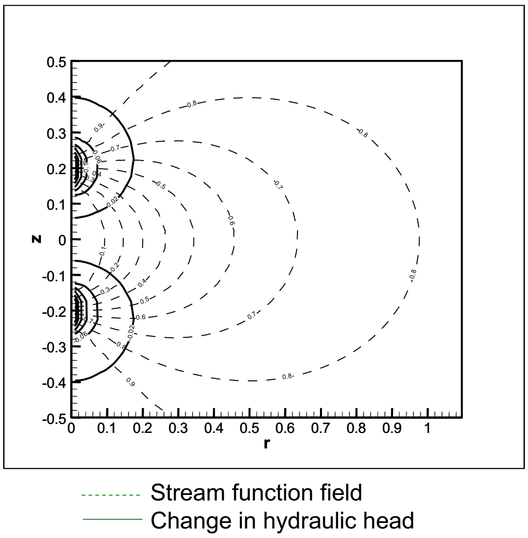
Goal: To develop a numerical multi-phase reactive transport model that interprets breakthrough curves obtained from a dipole flow and reactive tracer tests

- Accurate
- Flexible
- Robust
- Extendable

Numerical Model: Components

- Steady-state ground water flow component
- Transient aqueous phase reactive transport component
- Reactive solid phase matrix component

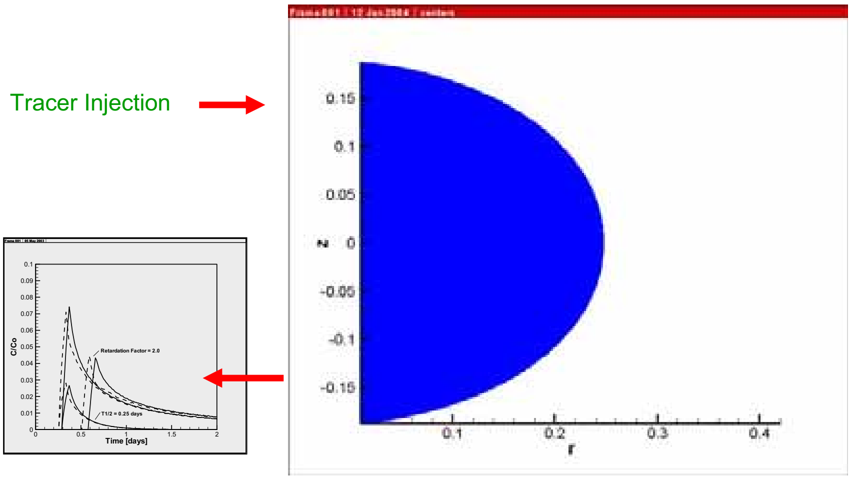
Numerical Model



Dipole Configuration:
L = 0.200 m
Δ = 0.050 m
r_w = 0.010 m
Q = 6.667×10^{-7} m^3/s

Aquifer Properties:
K_r = 1×10^{-5} m/s
K_z = 1×10^{-5} m/s
ϕ = 0.33

Numerical Model: Results



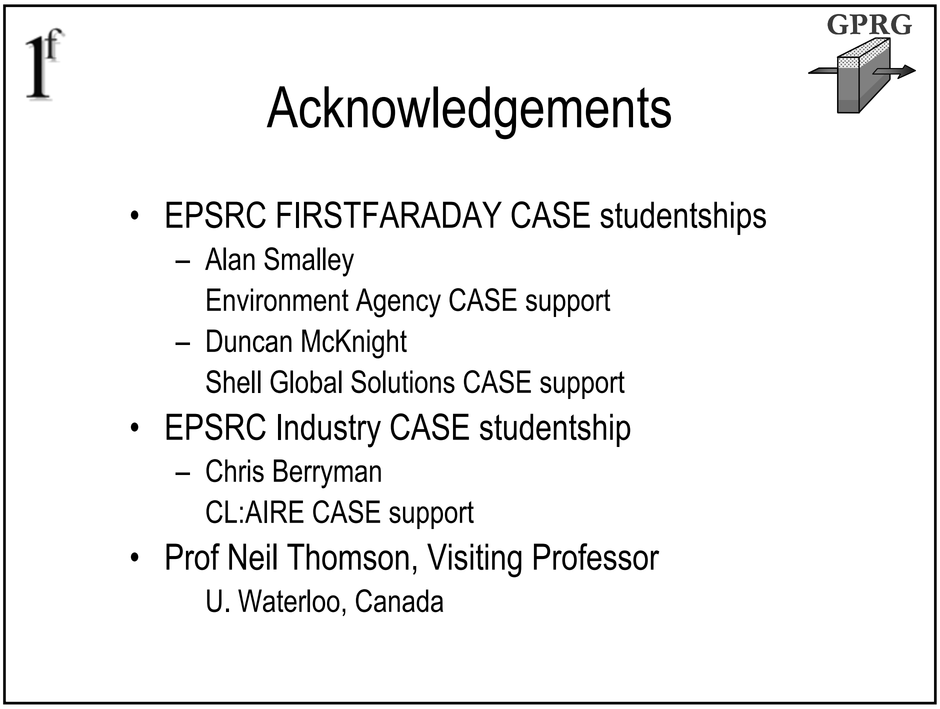
Tracer Injection

——— Advective BTC for a conservative, sorbing (*R*=2.0) and decaying($T_{1/2}$ = 0.25 days) tracer using Z&L equations

--------- Using numerical solution

Summary

- Motivation for research is the need to get contaminated sites back into use
- MNA is cheaper to “run” but has up-front costs
- Need better methods to collect data for site models
- Have started a step-wise research programme
  - Flow and transport calculations help design lab tests
  - Lab testing will move to full-scale tests at SIReN site
  - Numerical model evaluates site parameters
  - Will be linked to Site Investigation Cost-Benefit Analysis
  - Will be linked to MNA Risk Calculator



Acknowledgements

- EPSRC FIRSTFARADAY CASE studentships
  - Alan Smalley
    Environment Agency CASE support
  - Duncan McKnight
    Shell Global Solutions CASE support
- EPSRC Industry CASE studentship
  - Chris Berryman
    CL:AIRE CASE support
- Prof Neil Thomson, Visiting Professor
    U. Waterloo, Canada

CBA Calculator

Aims

- Review of Site Investigation Method Selection Tools
- Catalogue of Parameters
- Catalogue of Techniques
- Construct Tables of Parameters and Techniques with respect to properties of each
- Database construction
- CBA calculator

Review of Site Investigation Method Selection Tools

- What tools are available?
- How comprehensive are they?
- Strengths/weaknesses of presentation?

Findings of Review

- Weighted towards one aspect of SI
    - e.g. mainly include analysis techniques *OR* intrusive techniques
    - Concentrates on traditional techniques *OR* newer techniques
    - Few mention other parameters such as K_d or porosity
- Some are simplistic
- Others more complex and flexible, though outputs are generally less helpful than they could be

Aims for the current tool:

- Flexibility
    - search with regard to a parameter, a range of parameters or a particular technique
- Filter suggestions
    - By maximum depth of investigation
    - By site conditions
    - By time requirements
    - By site access requirements
- Produce a coherent strategy
    - From sampling through to analysis for a particular level of investigation
- Allow direct comparison between techniques

Catalogue of Parameters

- Taken from UK guidance and risk models:
    - e.g. Published and forthcoming SGV reports
    - e.g. Published and forthcoming TOX reports
    - UK risk assessment models:
        - CLEA
        - SNIFFER
        - CONSIM
        - P20
        - MNA Protocol

Catalogue of Techniques

- From ‘official’ method sources
    - e.g. EA ‘blue books’ for water analysis
    - US EPA solid waste methods
- British Standards
    - Intrusive investigation and sampling
- From ‘innovative’ method sources
    - e.g. US TIO website

CBA

- 2 Parts:
    - Database of parameters and methods
        - Relational database allows intelligent interrogation of the information allowing a more flexible tool
        - Allows web-based facility
        - Allows easy updating
    - CBA Calculator
        - DB allows simple calculations
        - Export for more complex approaches e.g. into spreadsheet

CBA Database

- Tables – used to design a database structure
- Database – will provide the ultimate CBA calculator with the appropriate data/manipulation
  - Simple calculation
  - Statistical methods
  - Neural Network
  - Others?

CBA Database

- A series of tables were constructed:
  - Parameters
  - Sample Access e.g. drilling techniques
  - Sample Collection – methods of sampling
  - Sample Analysis

Database Structure:

spreadsheet vs database

- Spreadsheet
  - Large – spread over several sheets, duplicated data
  - Complex
  - Searching – simple but cumbersome
- Database
  - Easier to update – using prepared forms
  - Potentially complex
  - Stand alone (especially if web-based)
  - Allow more focussed searches

CBA Calculator

- Give alternatives when ‘standard’ site questions have been answered
  - e.g. maximum depth of the investigation
    what matrices need to be sampled
    parameters which need to be measured
    quality of parameter measurement
- Use data from the selected options to assess the investigation

CBA Calculator

- Calculation Options
  - Simple calculation
  - Statistical – e.g. probability functions
  - Neural Networks
  - Fuzzy Numbers?
- Calibration
  - Compare with CBA response?
  - Train neural net?

CBA Questions

- Representing Data Quality of Measurement:
  - How to assess whether a technique’s data is “quantitative” “semi-quantitative” or “screening” quality etc
  - How to include LOD, precision, bias etc
- How to represent cost
- Representing sample quality

Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

Development of an In Situ Aquifer Assessment Tool

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ABSTRACT

Monitored Natural Attenuation (MNA) has become an effective alternative to interventionist remediation methods for the in situ treatment of contaminated groundwater. This low-cost technology requires a high degree of certainty in the conceptual site model and the underlying reactive transport processes. In order to gather site specific information, site characterization studies must be performed; however, the expense of these studies detracts from the low-cost nature of MNA. Additionally, existing aquifer assessment methods, which range from simple laboratory batch and column studies of environmental samples to large-scale plume studies, suffer from several disadvantages. These include the likelihood that the small sample cores are not representative of the heterogeneous subsurface system, the disturbance and possible contamination of cores during collection, the inability to reproduce the exact in situ condition in the laboratory, and the long required time frame. Hence, cost-effective site characterization techniques are required which provide a level of information suitable for demonstrating that in situ processes are present for MNA to be a viable treatment option. Development of such techniques can not advance without integrating the latest technology in several different research areas such as laboratory methods, field techniques, groundwater mathematical, numerical, and inverse modeling techniques, management and optimization systems, as well as cost-benefit studies to show when more sophisticated techniques are most useful.

Introduction

The dipole flow field was originally applied in the late 1980s to remediate contaminated ground water by injecting into one depth interval and extracting from another depth interval of a single well. The extracted water was either treated by air stripping within the well, or amendments (e.g., oxygen, nutrients, or chemicals) were added to the extracted water before it was re-injected. Herrling and Stamm (1992) were one of the first to investigate the general features of vertically circulating flow fields in support of their use as a remedial technology.

In an attempt to develop a dependable low-cost site characterization technique, the dipole-flow test, developed by Kabala (1993), is extended to include reactive tracers so that in situ reactive parameters required to support MNA can be estimated. This site characterization test is called The Dipole Flow Reactive Tracer Test (DFRTT). The DFRTT could be described as a column experiment of an undisturbed uncontaminated large scale field sample. The key concept of the DFRTT is to characterize the subsurface using the fewest number of field tests by employing the latest innovations of science, engineering, and technology. This would lead to major benefits in both time and value for money. Most existing site investigation tools simply fail to provide relevant data, thereby resulting in unnecessary uncertainty.

A team of researchers from different disciplines including earth scientists, mathematicians, modellers, engineers, chemists, biologists, field managers, as well as laboratory experts are working together to develop and enhance such new technology. The objective is to improve the risk based assessment of contaminated groundwater through the development of the DFRTT as a reliable cost effective method of site specific characterisation of reactive transport properties supported by a cost/benefit calculator that will provide decision support to enable site investigation designers determine when to deploy the DFRTT. We term this methodology the In Situ Aquifer Assessment Tool (AAT) (Fig. 1). This tool injects water with multiple tracers in one packered section of a borehole, and observes their breakthrough curves in a pumped section of the same borehole. The cost/benefit calculator provides quantitative decision support and guides when to use the tool.

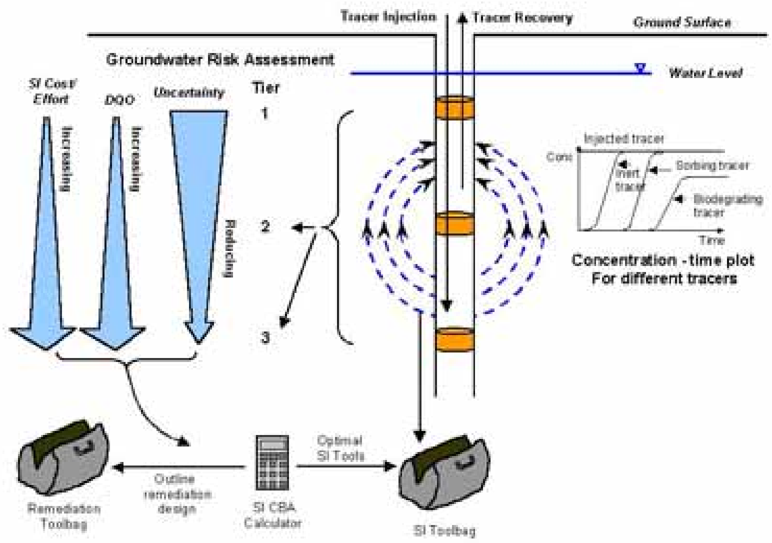


Fig.1. The DFRTT as an In Situ Aquifer Assessment Tool

This project consists of four related major components. Firstly, a DFRTT sandbox-scale physical model will be built and used to verify theory. Secondly, a numerical multi-phase reactive transport model describing radial flow introduced in DFRTT will be developed. A complete field study including tracer tests at the SIReN site represents the third component. Finally, a cost/benefit analysis calculator will be developed and tied to the DFRTT for the purpose of advising site investigation designers on when to commission the DFRTT as part of the decision to possibly implement MNA.

Laboratory-scale experiments

The sandbox physical dimensions are determined by the radial extent of the flow generated by the dipole probe. Hantush (1964) and Zlotnik and Ledder (1994) numerically modelled the dipole flow patterns within a vertical circulation well at steady-state in an unconfined, infinite aquifer and provided the following approximations for the physical extent of a dipole flow field:

Minimum horizontal extent of flow = 10aL (20aL diametrically) (1)
Minimum vertical extent of flow = 4L (8L diametrically)

where L is the half-chamber separation (or shoulder length; exactly half the distance between chamber centres), and a is the anisotropy ratio (a^2 = Kr/Kz, the ratio between the horizontal and vertical hydraulic conductivities). Therefore, a model dipole probe with a shoulder length of 10 cm in an isotropic medium would generate a flow field with a radius of 1m and would require a sandbox 2 m in diameter in order to minimise boundary interference. Also, the same flow field would extend to ±40 cm from the centre of the dipole probe. A sandbox of dimensions 2 m x 2 m x 1 m is constructed (Fig.2) with the dipole probe (shoulder length not greater than 10 cm) located in a central well. Laboratory-scale trials will not only support the development of the test in the field, but will also provide useful datasets for development, testing and calibration of the numerical model.

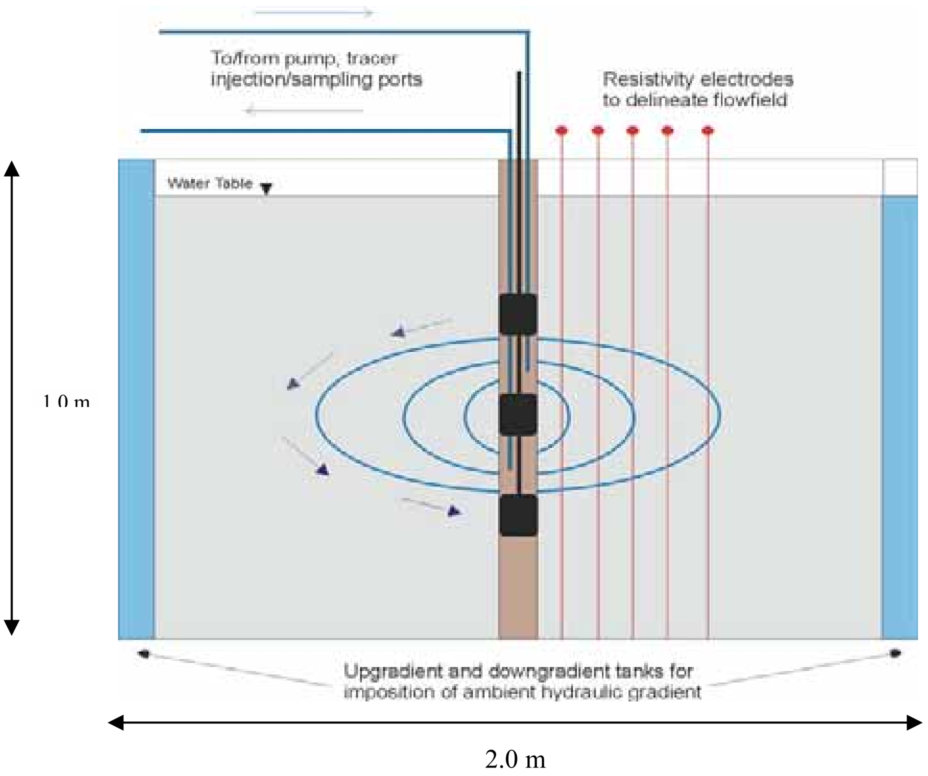


Fig. 2. Configuration of the sandbox and the dipole test assembly

Field-scale experiments

Field trials of the DFRTT will take place at SIReN located at a large petro-chemical complex in Greater Manchester. Design of the field experiments is governed largely by the need to recover a suitable amount of tracer in a relatively uncharacterised porous media and also the need to choose a suitable test venue within this large site. The field apparatus will consist of a series of three inflatable packers that hydraulically isolate an injection test zone from an extraction test zone and the aquifer above/below the assembly (Fig 2). The length of the test zones will be determined by the results of the lab-scale model experiments and numerical modeling and practical constraints of construction in the field. However, the extraction test zone will be located above the injection test zone in the assembly. Predictive modelling indicates that the field-scale DFRTT will produce breakthrough curves (BTCs) of usable quality provided that significant fractures and layers can be avoided.

Numerical model

The DFRTT would not fulfil its potential as an Aquifer Assessment Tool without being accompanied by a numerical model that interprets the specific data required for site investigation and, therefore, increases the applicability of the tool. A multi-phase reactive transport numerical model that can be used to interpret BTCs obtained from a DFRTT is currently under development. The model consists of three major components: a steady-state ground water flow component, a transient aqueous phase reactive transport component, and a reactive solid phase matrix component. This model accounts for well skin effects with a user specified thickness, hydraulic conductivity, and porosity; provides options for the location of upper and lower horizontal boundaries; allows for a user specified location of a horizontal feature with a thickness, hydraulic conductivity, and porosity; and accounts for an asymmetric dipole system. This model is designed to be able to provide an accurate representation of the first-order processes; conform to a variety of field configurations and conditions; computationally handle a range of input parameters; and be extendable so that additional reactions or processes can be added to the model as required with minimal coding effort.

Cost/benefit analysis calculator

The choice of site investigation methods becomes ever more complex with new on-site, in-situ (such as AAT) and laboratory based methodologies being developed continuously. In order to facilitate the choice of site investigation techniques, a catalogue of available drilling, sampling and analysis techniques has been constructed. This includes details of aspects such as what parameters are measured, to what degree of certainty and for which medium as well as relative costs. Linked to this, a cost-benefit calculator will be constructed in order to return the resolution of measurement required for each parameter at a particular risk assessment tier and ultimately give guidance on the final choice of method with respect to cost. This will allow the design of site investigations to deliver the required quality of data to support decision making in either the risk assessment or the remediation design or verification stages of a project. The initial phase of the CBA calculator will focus on characterising groundwater and a second phase will extend this to soil characterisation as well. The CBA calculator will sit alongside existing guidance on how many samples to take and where to take them. It is intended to answer the question of what to measure and how to measure it as opposed to where to measure.

REFERENCES

Hantush MS, 1964. Hydraulics of wells. Advances in Hydroscience, vol. 1, (edited by V.T. Chow) 281-432, Academic, San Diego, California.

Herrling, B., and J. Stamm. 1992. Numerical results of calculated 3D vertical circulation flows around wells with two screen sections for in situ or on-site aquifer remediation, Computational methods in Water Resources IX.

Kabala, Z. J. 1993. The Dipole flow Test: A new single-borehole test for aquifer characterization, Water Resour. Res., 29(1), 99-107.

Zlotnik, V. A., and G. Ledder. 1994. Effect of boundary conditions on dipole flow, In Computational Methods in Water Resources X, Vol. 2, ed. A. Peters et al., Norwell Mass., Kluwer Acad., 907-914.

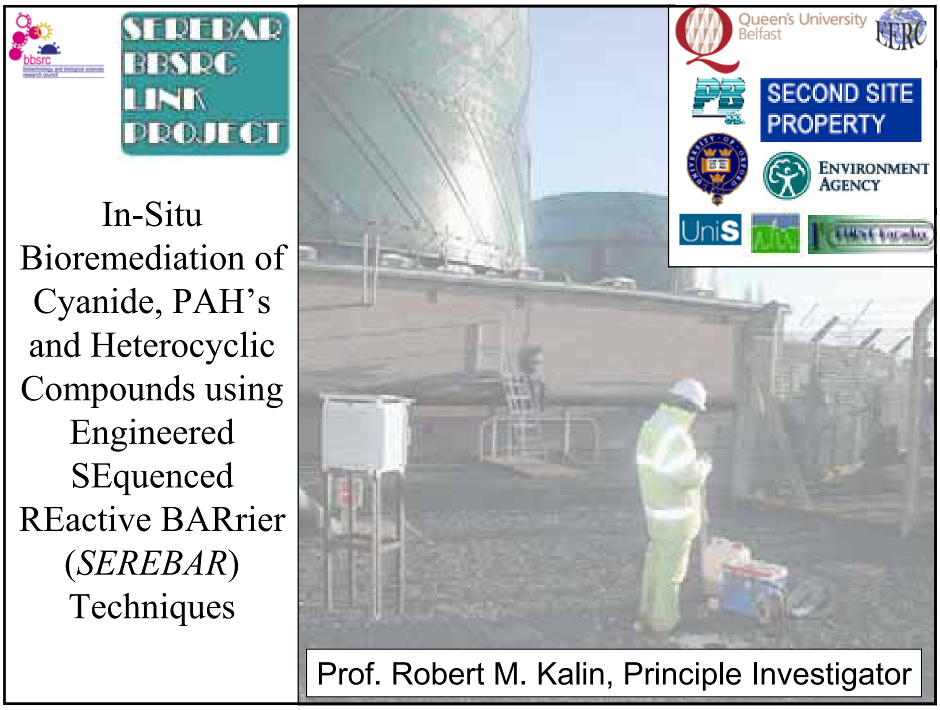
Biographical Note

Professor Robert Kalin

Robert Kalin is Professor of Environmental Engineering at The Queen's University Belfast. He is actively involved in research on contaminated land remediation, groundwater geochemistry, and on the use of stable isotopes in soil and groundwater as an indication of contaminant degradation. His research interests include the use of chemistry and isotope geochemistry to better understand natural water systems and man's impact on the global environment. Professor Kalin's laboratory is actively involved in international research on the use of isotope geochemistry for the understanding of groundwater flow dynamics and contaminant transport in both groundwater and surface water.

In-Situ Bioremediation of Cyanide, PAHs and Heterocyclic Compounds using Engineered SEquenced REactive BARrier (SEREBAR) Techniques

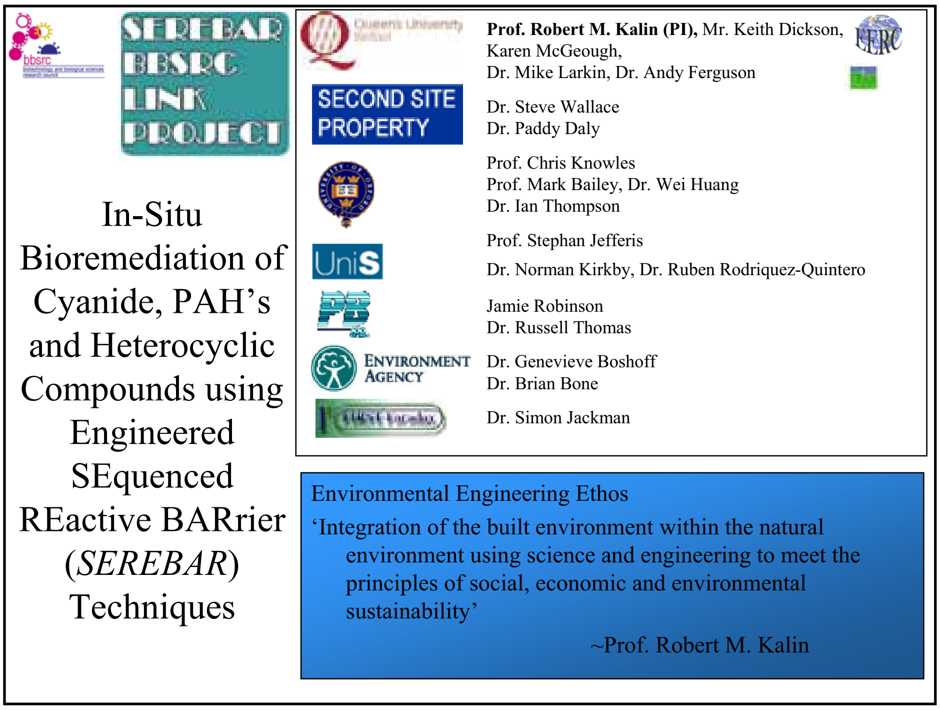
Robert Kalin



SEREBAR BBSRC LINK PROJECT

In-Situ Bioremediation of Cyanide, PAH's and Heterocyclic Compounds using Engineered SEquenced REactive BARrier (*SEREBAR*) Techniques

Prof. Robert M. Kalin, Principle Investigator



SEREBAR BBSRC LINK PROJECT

In-Situ Bioremediation of Cyanide, PAH's and Heterocyclic Compounds using Engineered SEquenced REactive BARrier (*SEREBAR*) Techniques

Prof. Robert M. Kalin (PI), Mr. Keith Dickson, Karen McGeough,
Dr. Mike Larkin, Dr. Andy Ferguson

Dr. Steve Wallace
Dr. Paddy Daly

Prof. Chris Knowles
Prof. Mark Bailey, Dr. Wei Huang
Dr. Ian Thompson

Prof. Stephan Jefferis
Dr. Norman Kirkby, Dr. Ruben Rodriquez-Quintero

Jamie Robinson
Dr. Russell Thomas

Dr. Genevieve Boshoff
Dr. Brian Bone

Dr. Simon Jackman

Environmental Engineering Ethos

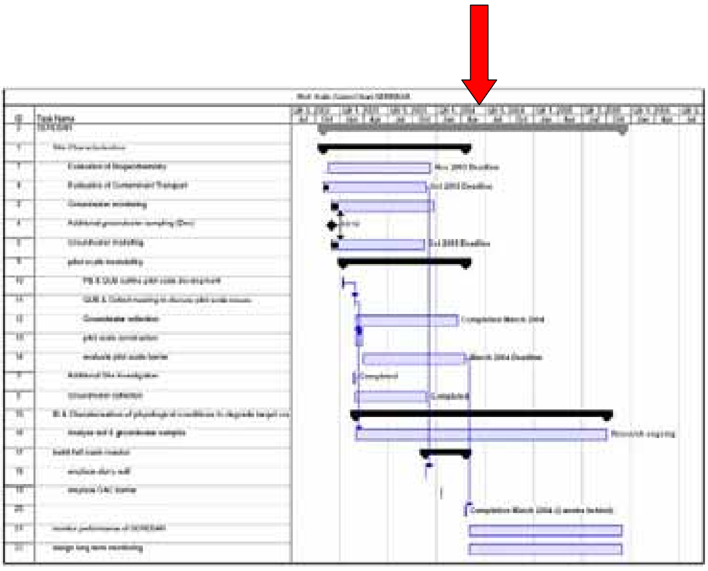
'Integration of the built environment within the natural environment using science and engineering to meet the principles of social, economic and environmental sustainability'

~Prof. Robert M. Kalin

SEREBAR
BBSRC
LINK
PROJECT

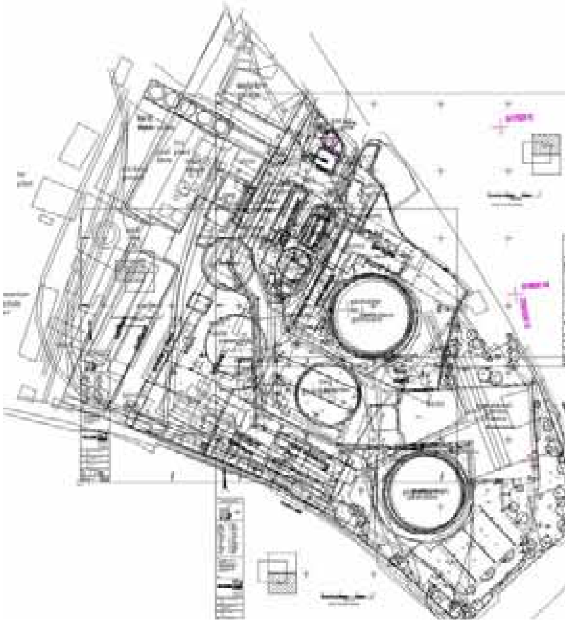
Project Management: Time Line

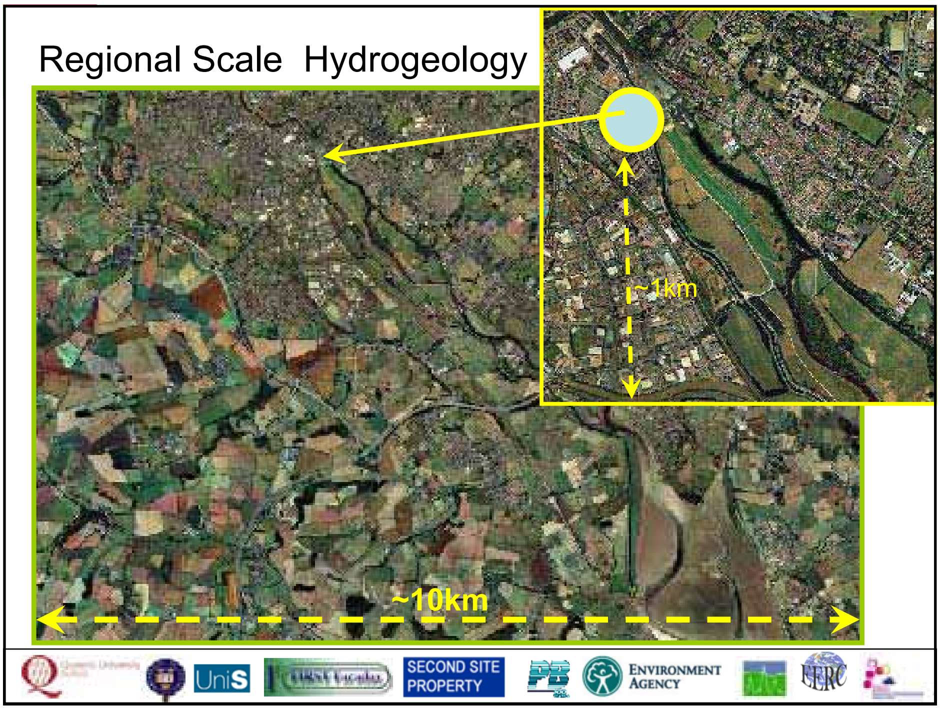
- 1 Nov 2002
- 1 Feb 2003
- 1 Jan 2004
- Now



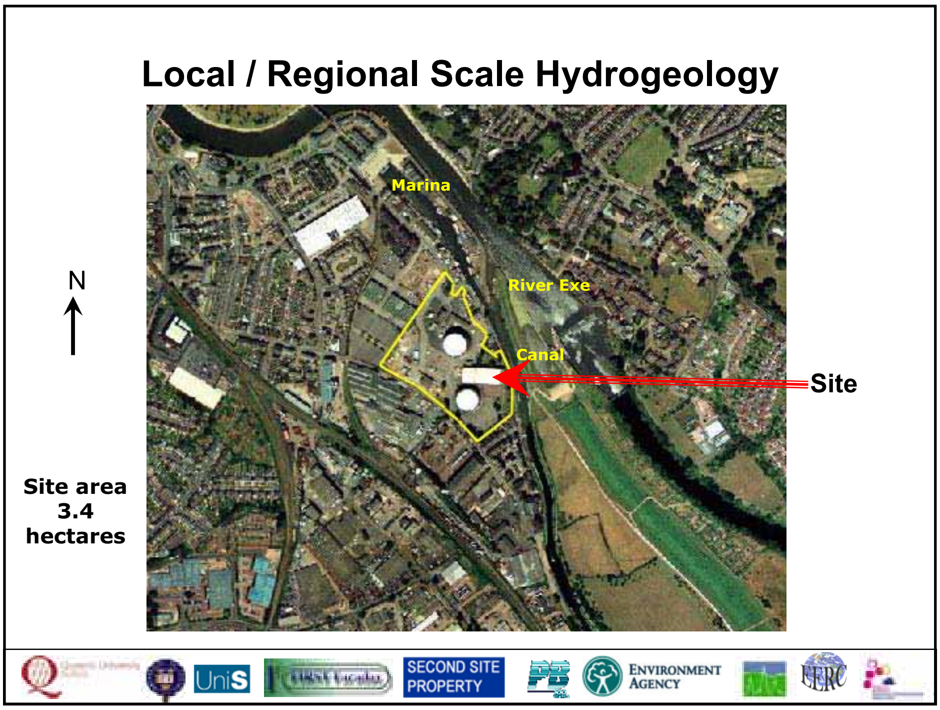
Site Selection

- **Active site use for significant period (>10yrs)**
- **Appropriate geology**
- **Appropriate risk drivers**
- **Appropriate risk management**
- **Feasibility**





Regional Scale Hydrogeology



Local / Regional Scale Hydrogeology

Site area 3.4 hectares

Local / Regional Scale Hydrogeology

- Site and Surrounding Area – Urban industrial, recharge through surface percolation greatly reduced due to impervious cover
- A series of weirs reduces river height north of the site
- Canal is fed from river and also marina immediately before weirs at river. Height of canal controlled by River Manager (~0.5m variance)
- Marina converted from an Ox-Bow lake; canal constructed in the 17th Century (Tidal Influence?)

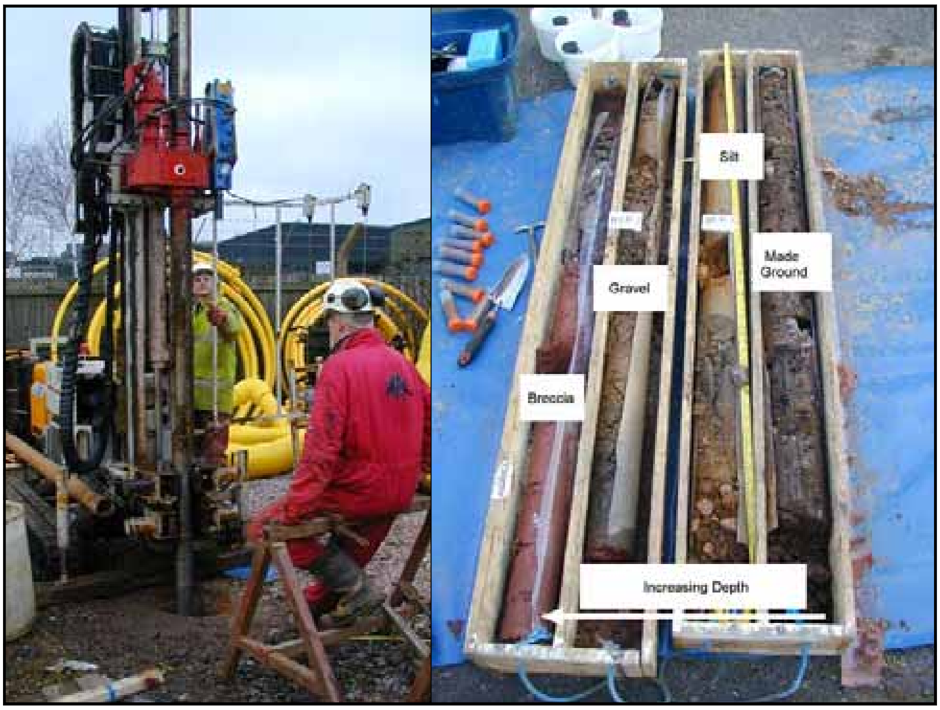
Site Specific Scale Hydrogeology

- **Adaptive Sampling, SI in the Field**

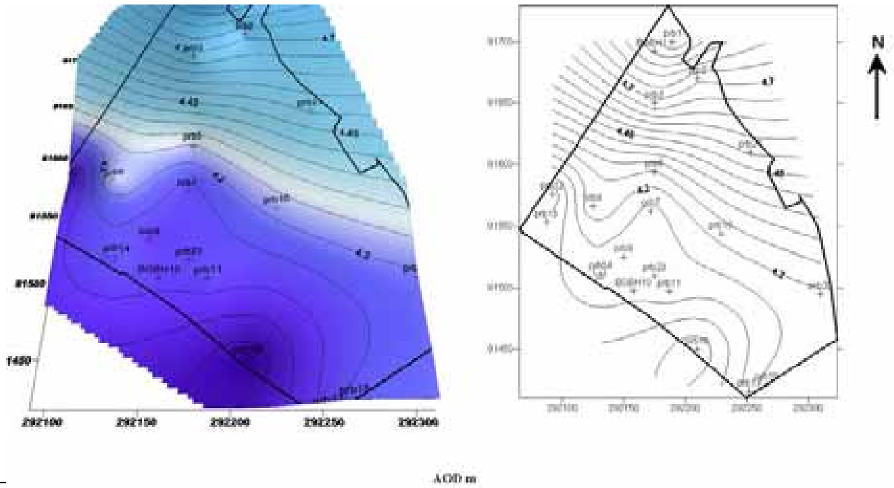
- Interpolation of lithologies
- Site geochemistry
- Measurement of groundwater over time
- Determination of hydraulic conductivities

In-Situ Bioremediation of Cyanide, PAHs and Heterocyclic Compounds using Engineered SEquenced REactive BARrier (SEREBAR) Techniques

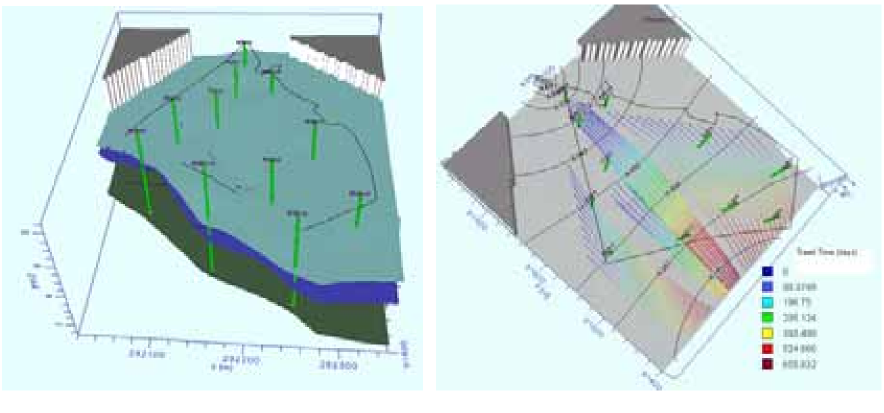
Robert Kalin

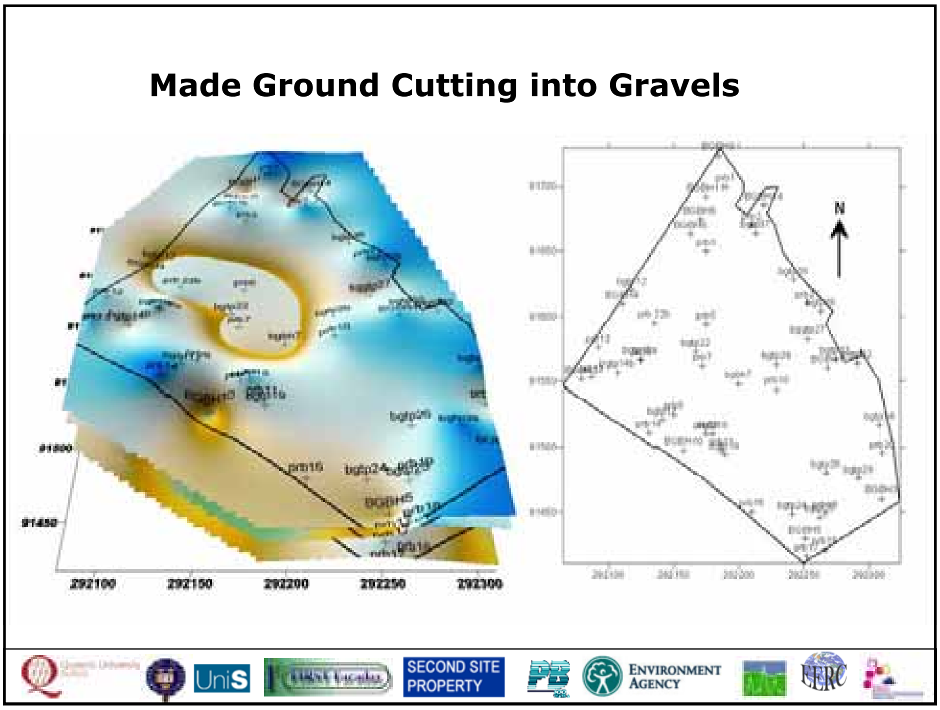


Initial Groundwater Conditions

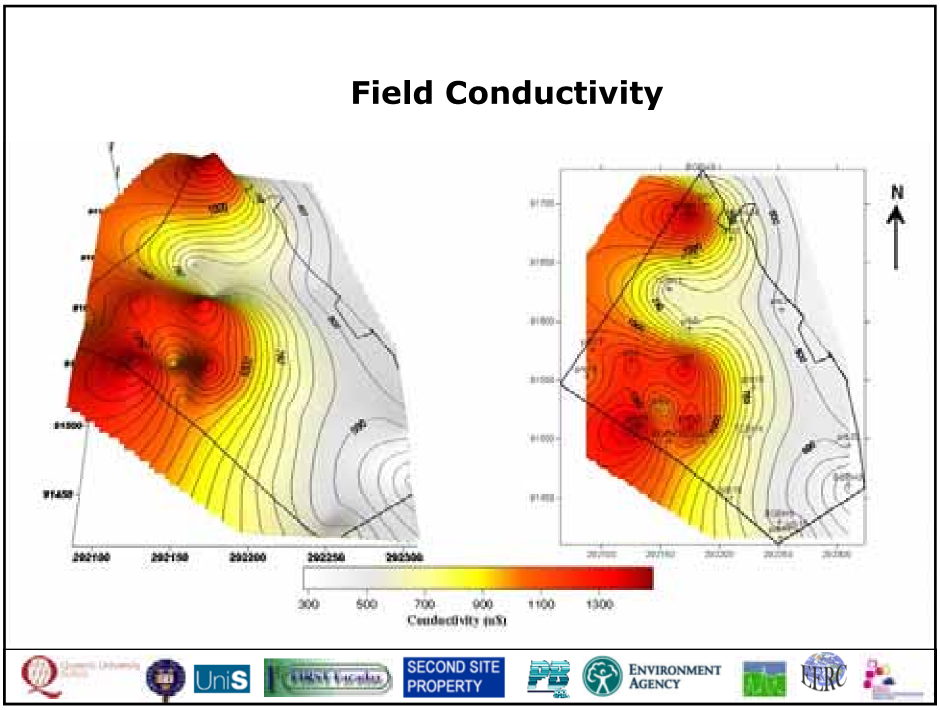


Adaptive Groundwater Modelling



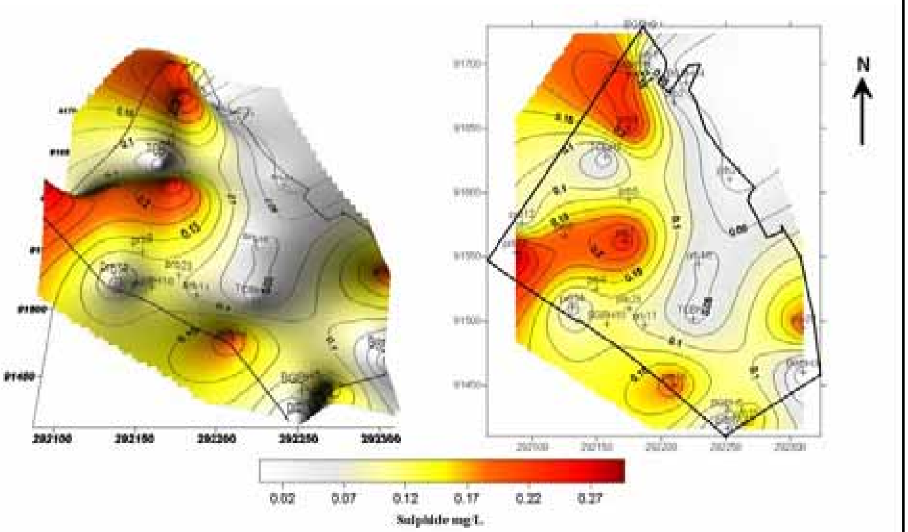


Made Ground Cutting into Gravels

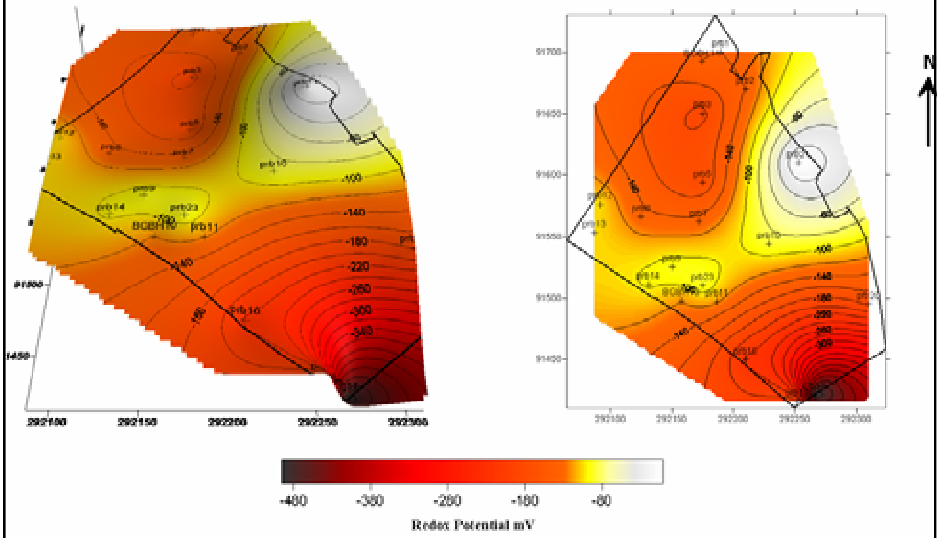


Field Conductivity

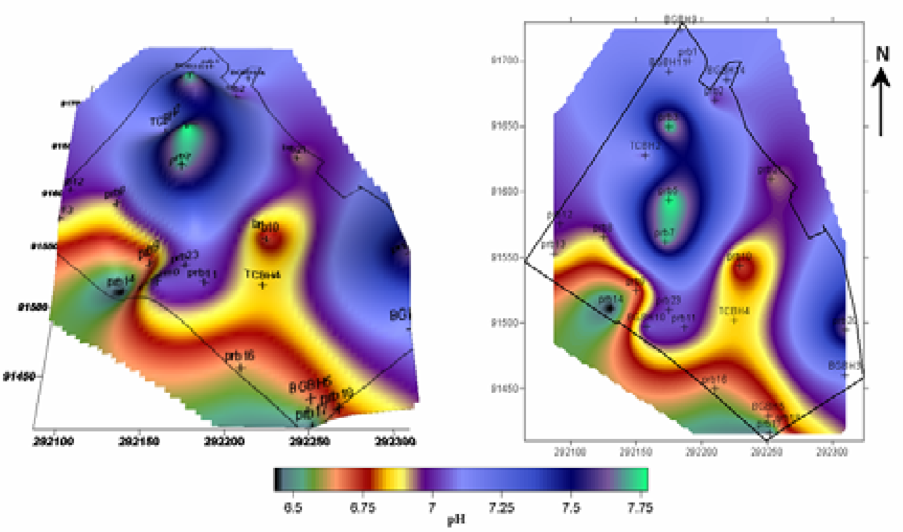
Sulphide



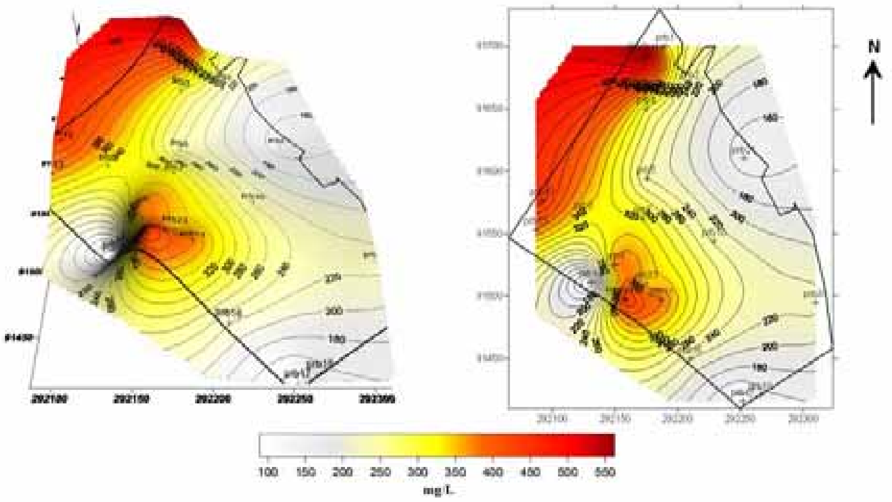
Redox Potential



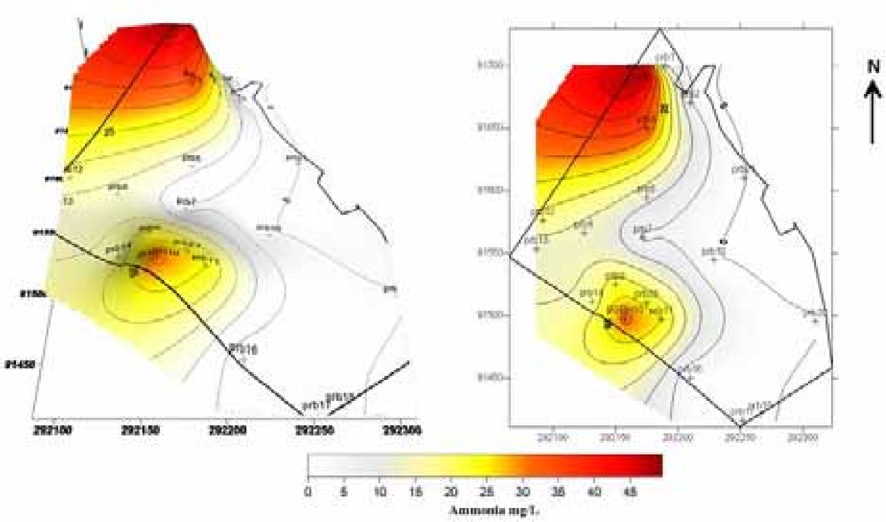
pH



Alkalinity



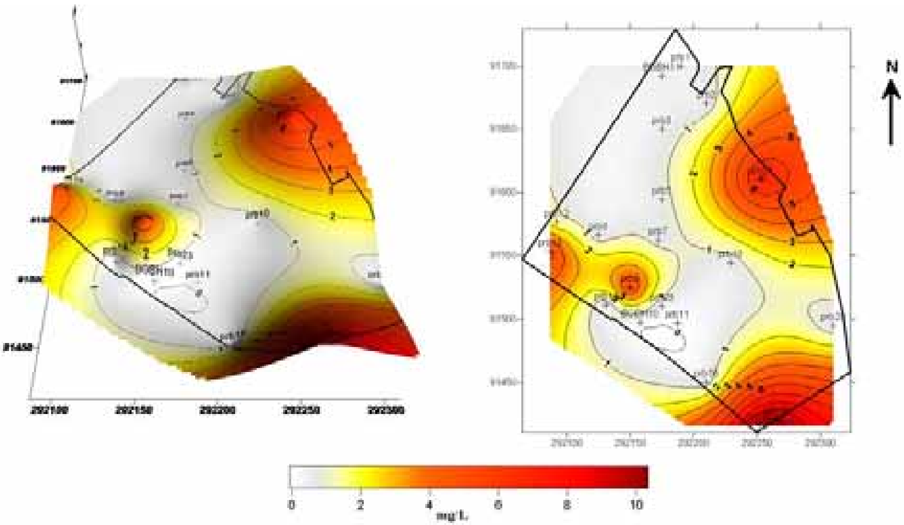
Ammonia



SECOND SITE PROPERTY

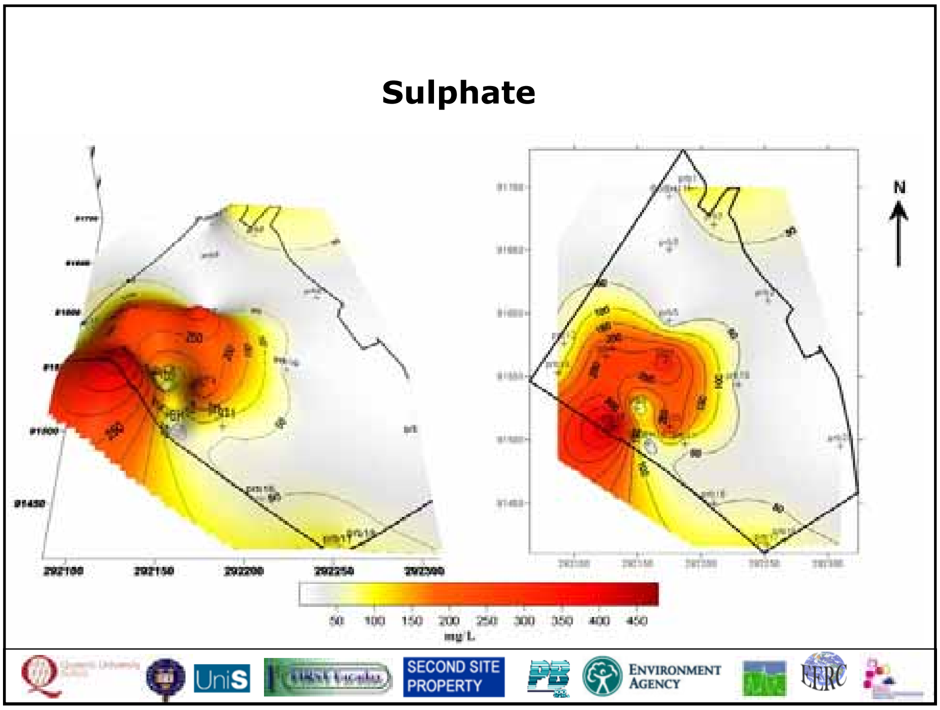
ENVIRONMENT AGENCY

Nitrate

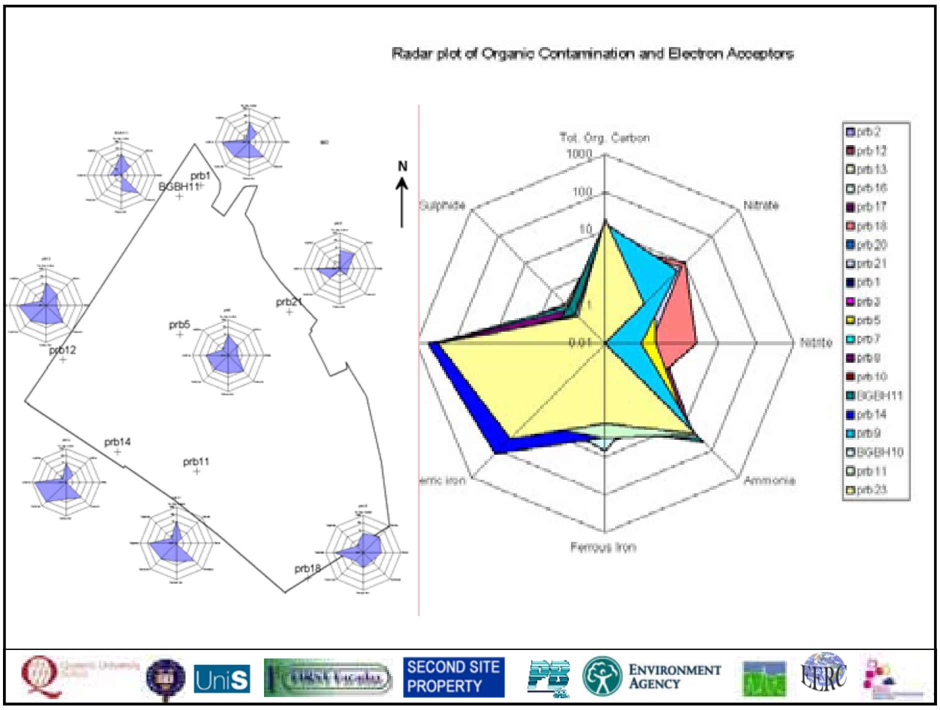


SECOND SITE PROPERTY

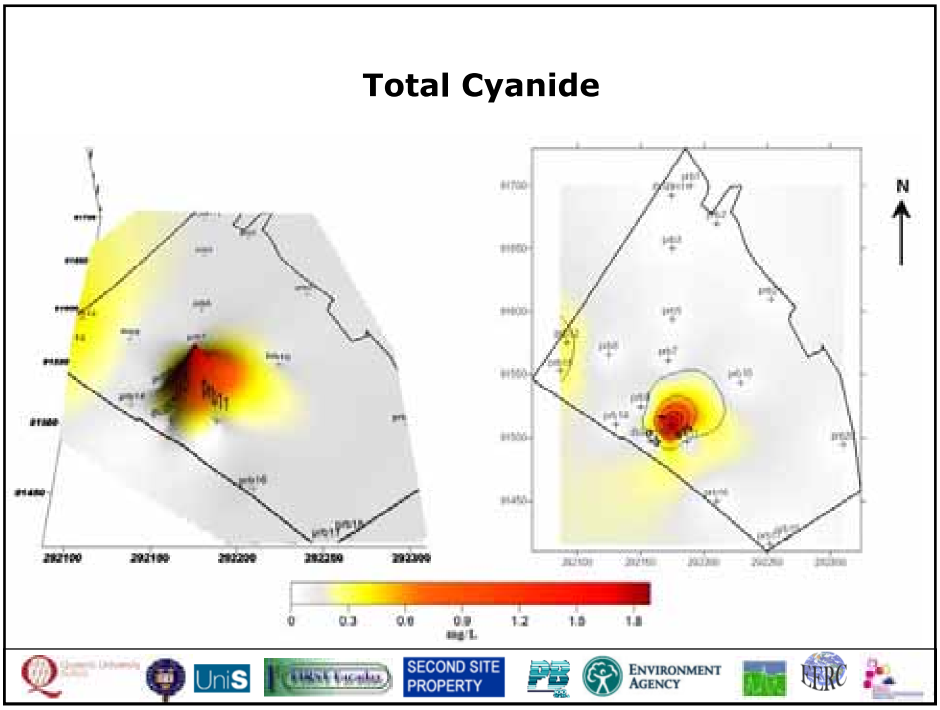
ENVIRONMENT AGENCY



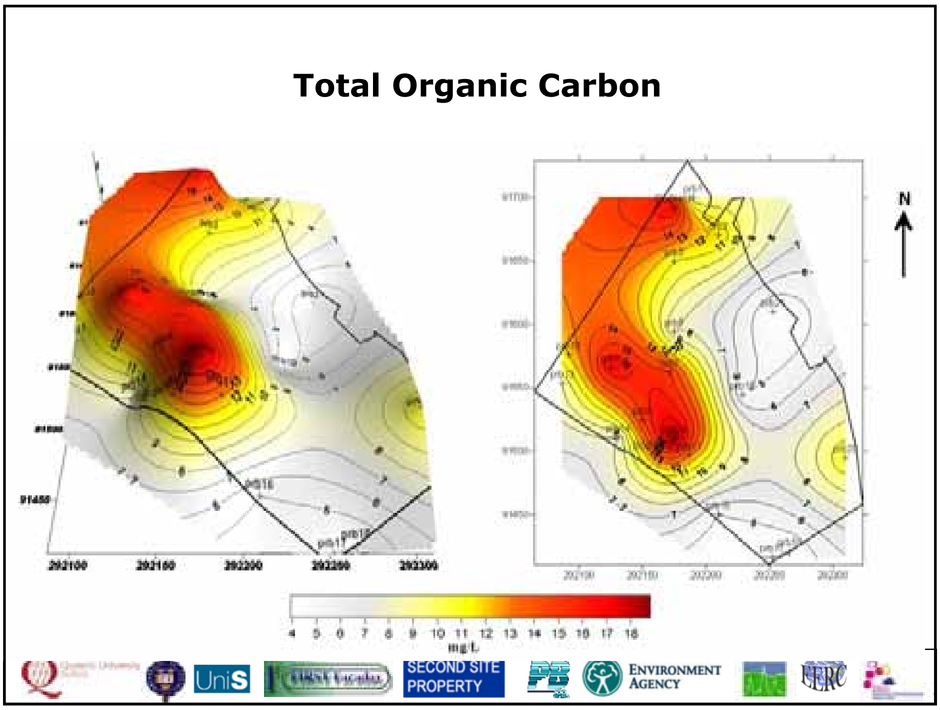
Sulphate



Radar plot of Organic Contamination and Electron Acceptors

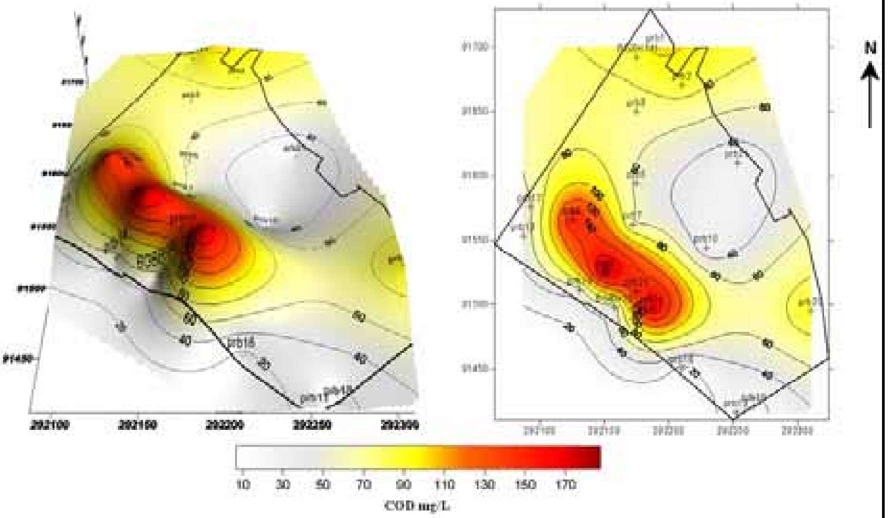


Total Cyanide

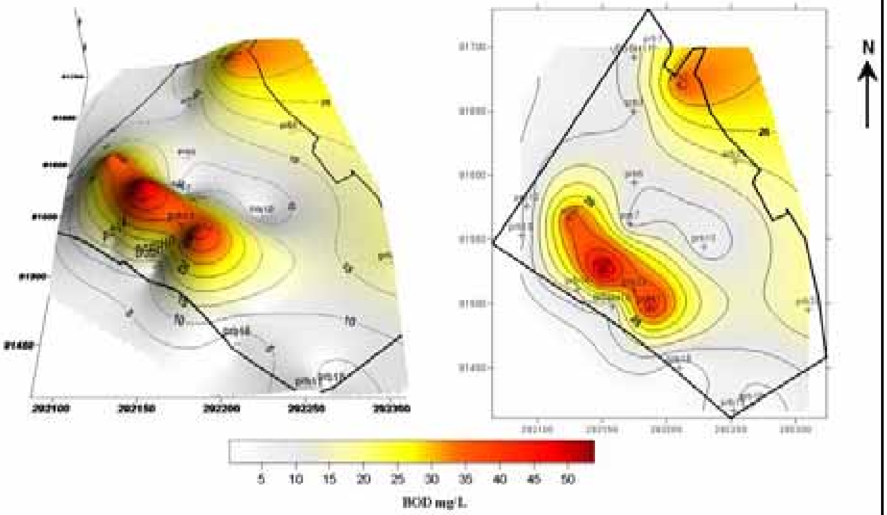


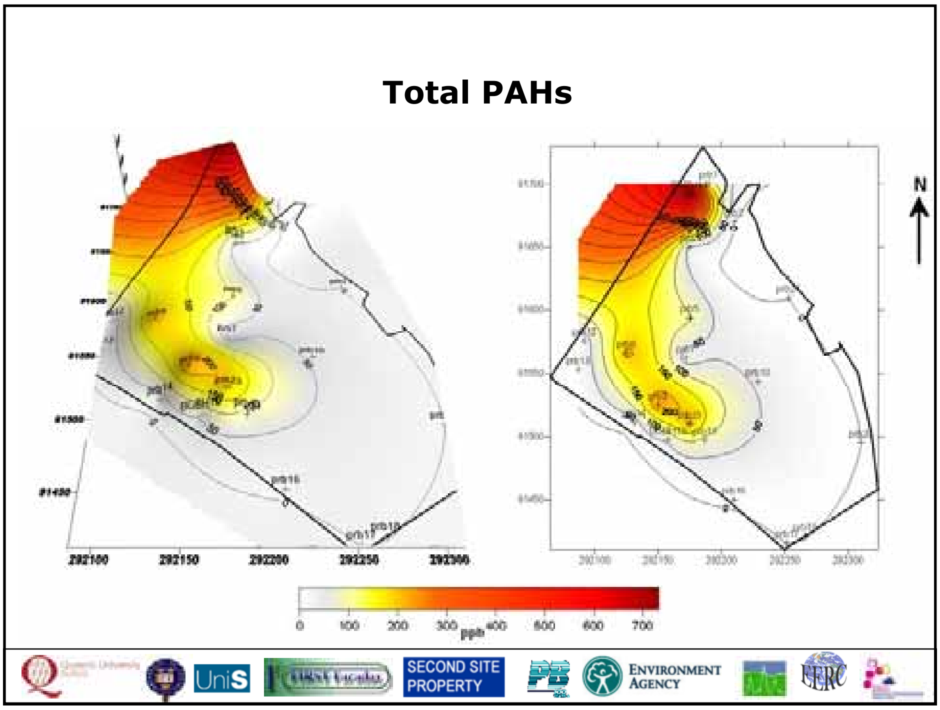
Total Organic Carbon

Chemical Oxygen Demand

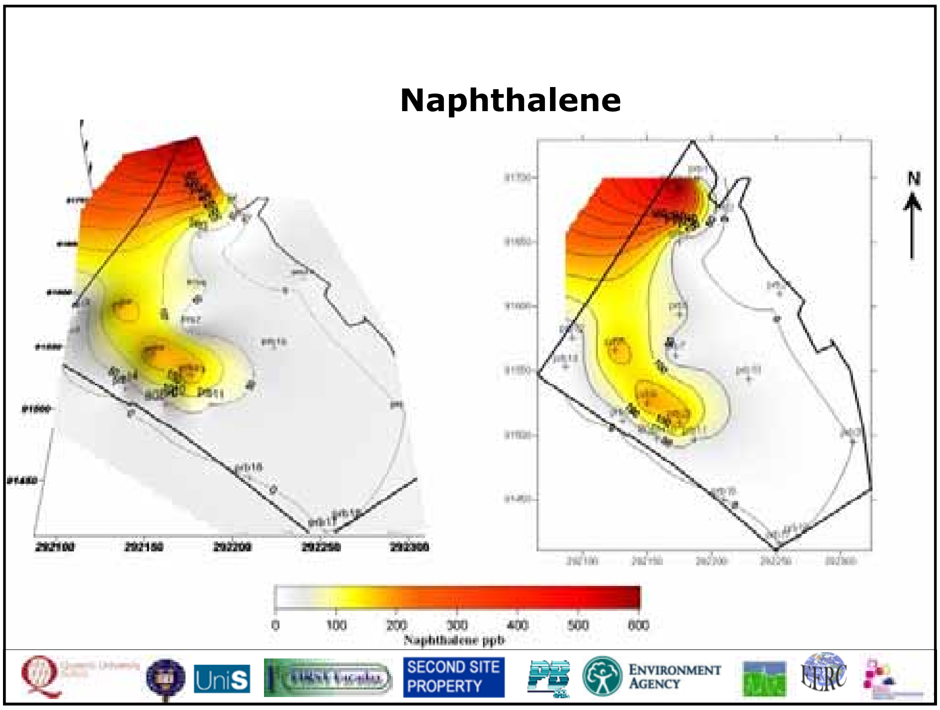


Biological Oxygen Demand



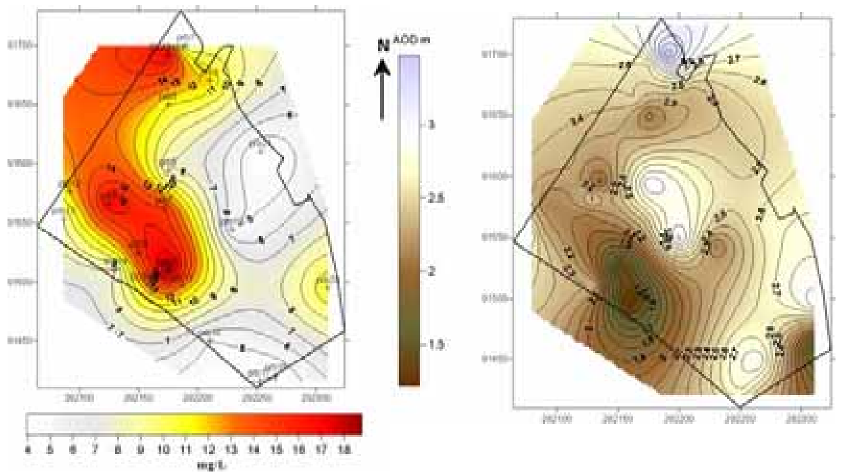


Total PAHs



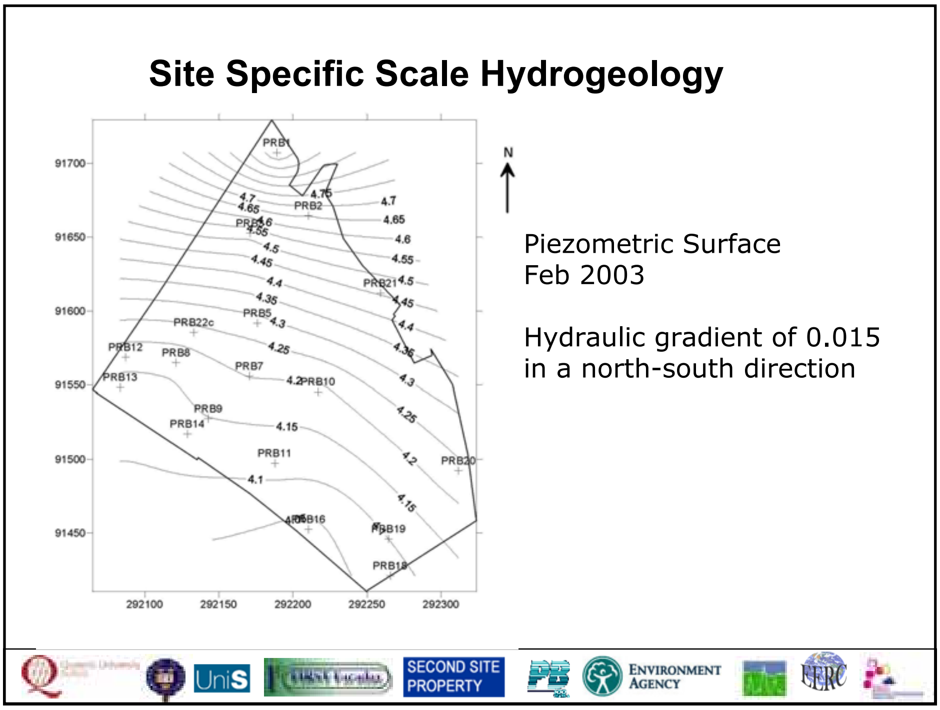
Naphthalene

TOC Plume & Base of River Gravels



Site Specific Hydrogeology Study

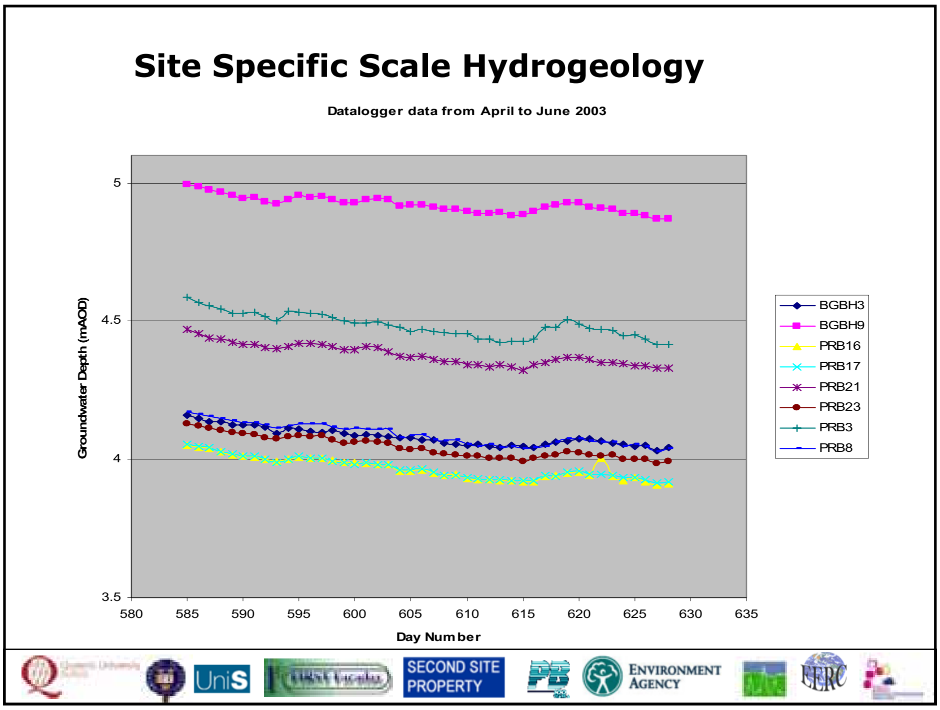
- Made Ground: Highly variable unsaturated zone
- River Terrace Lithologies:
  Silts – low permeability, generally above water table
  Gravels – Higher permeability, generally below water table
- Permian Breccia:
  Very Stiff, Very low permeability, weathered red clay



Site Specific Scale Hydrogeology

Piezometric Surface
Feb 2003

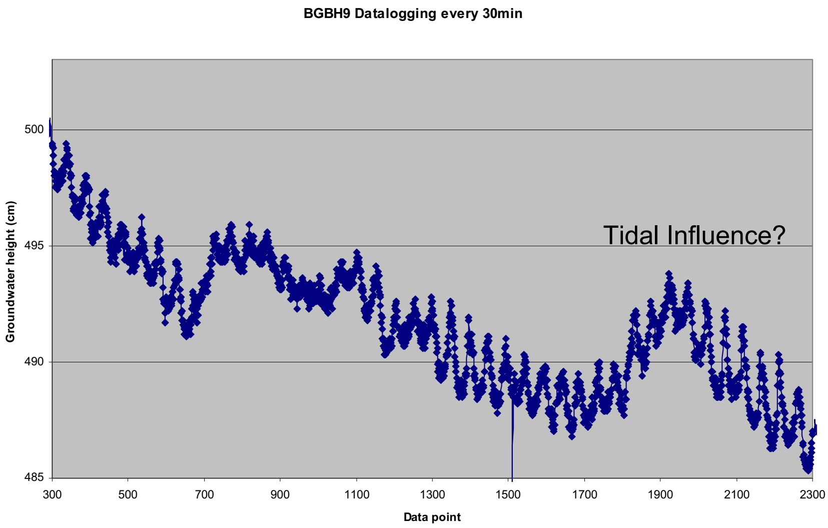
Hydraulic gradient of 0.015
in a north-south direction



Site Specific Scale Hydrogeology

Datalogger data from April to June 2003

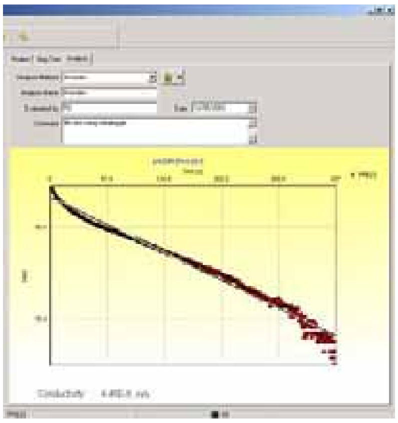
Site Specific Scale Hydrogeology



Site Specific Scale Hydrogeology

- Determination of Hydraulic Conductivities Across the Site
- Option of Pump Test or Slug Test
- Pump Test would require 1000Ls of contaminated groundwater to be disposed of. (Too Costly)
- Slug Test requires addition of a known volume to borehole to cause displacement and measurement of response using datalogger

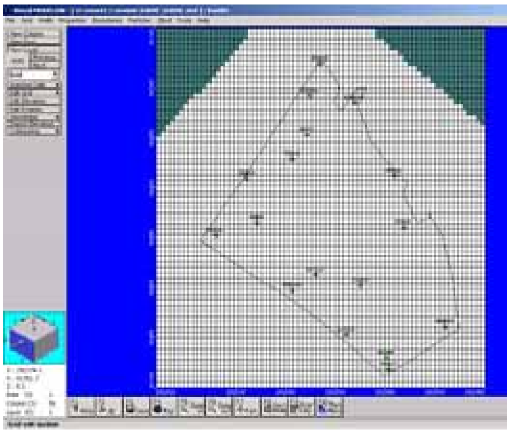
Site Specific Scale Hydrogeology



Well name	Bouwer & Rice (Conductivity m/s)	Hvorslev (Conductivity m/s)
PRB3	1.82E-5	2.49E-5
PRB7	2.45E-5	3.46E-5
PRB8	1.47E-5	2.25E-5
PRB13	1.13E-5	2.18E-5
PRB14	6.73E-6	9.36E-6
PRB16	1.22E-5	1.89E-5
PRB17	1.11E-5	1.79E-5
PRB21	1.07E-5	1.61E-5
PRB23	3.04E-6	4.46E-6
BGBH3	1.31E-5	1.77E-5
BGBH9	1.20E-5	1.53E-5

Numerical Model Development from Conceptual Model

- **Model grid Construction**
- **5m grid orientated in groundwater flow direction**
- **Grid extended as far as reasonable interpolation of lithologies & head allows**
- **Unconfined Aquifer, 1 layer used**

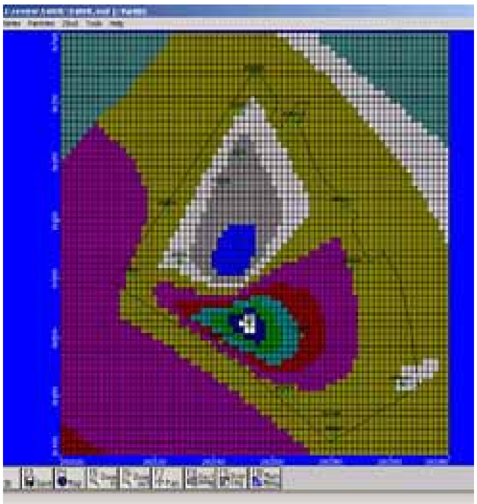


Numerical Model Development from Conceptual Model

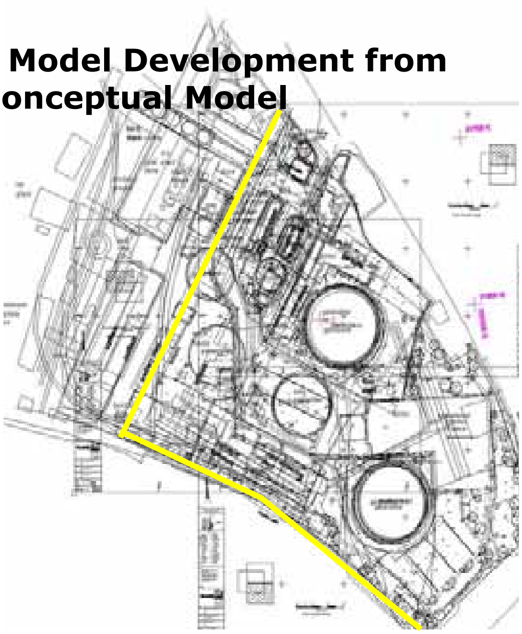
- **Model Properties**

  Hydraulic Conductivity Interpolated using

  Kriging
  Nearest Neighbour
  Inverse Distance



Numerical Model Development from Conceptual Model



•Areas of low or no groundwater flow due to foundations of structures (gasholding tanks etc.)

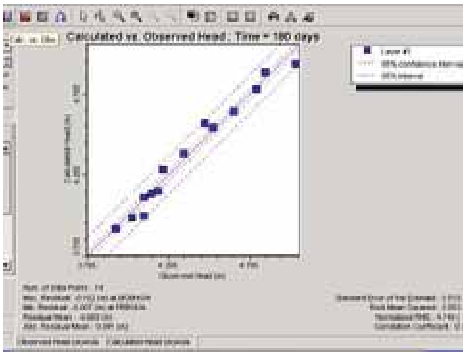
•Importance should be assigned to prior information

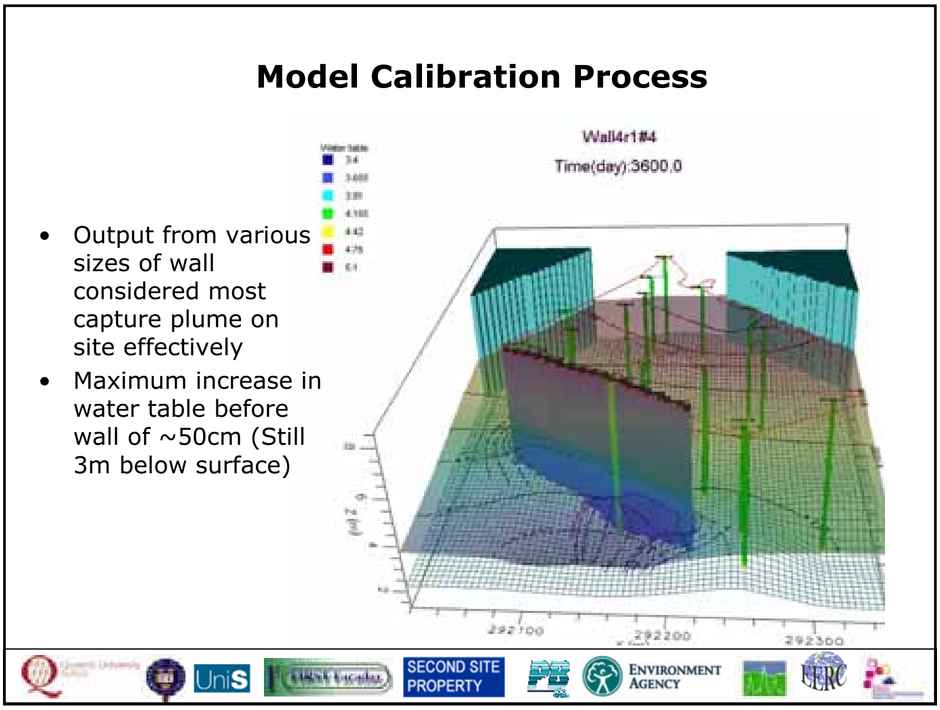
Numerical Model Development from Conceptual Model

- **Modelling Process**
- **An Evolving Sensitivity Analysis from simple to complex that initially correlates site data with modelled results (calibration) and eventually predicts reactions to external processes (i.e. us adding a slurry wall and reactive cell)**
- *"The methods of science depend on our attempts to describe the world with simple theories. Theories that are complex become unstable, even if they happen to be true. Science may be described as the art of oversimplification: the art of discerning what we may with advantage omit."*

Model Calibration Process

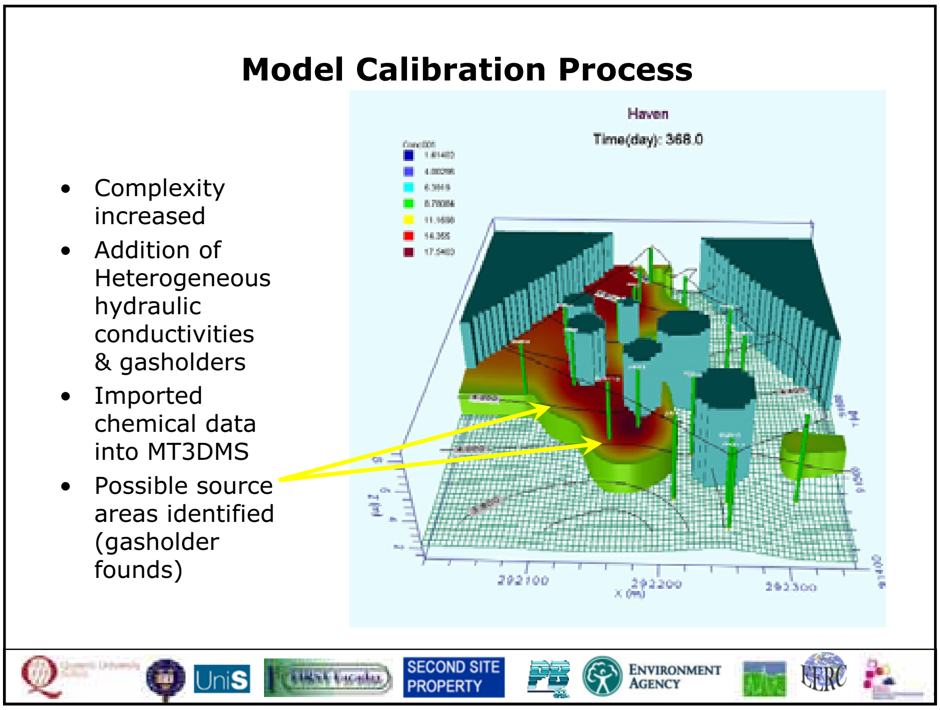
- Output from very simple model
- Hydraulic conductivity homogenous across site (2e-5m/s)
- Initial Heads from end of previous model run
- Run for 10 years
- Interactions with various sizes of slurry wall simulated
-





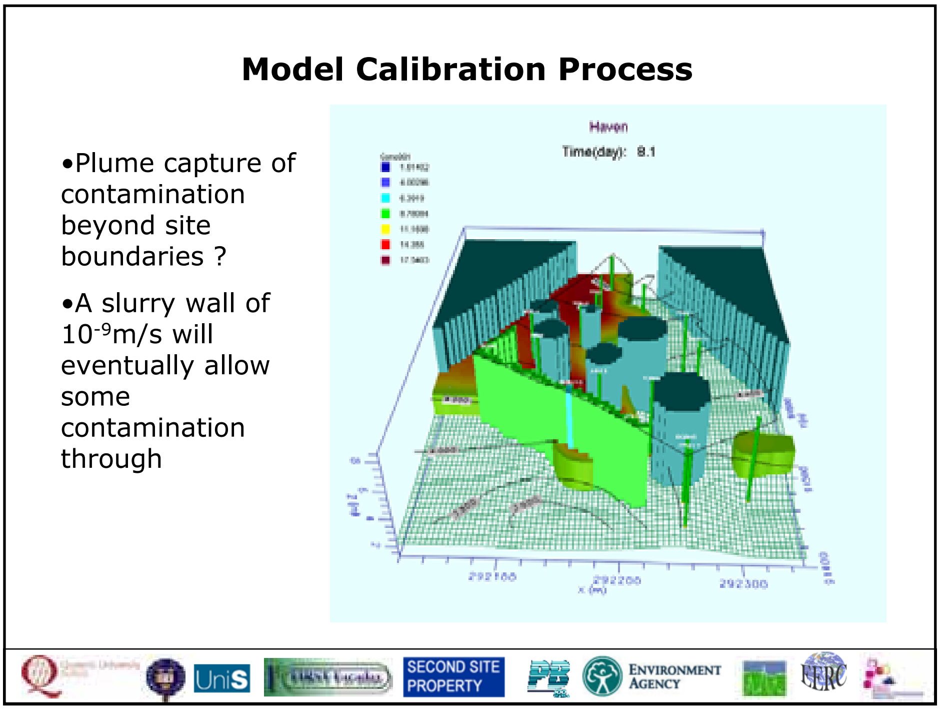
Model Calibration Process

- Output from various sizes of wall considered most capture plume on site effectively
- Maximum increase in water table before wall of ~50cm (Still 3m below surface)



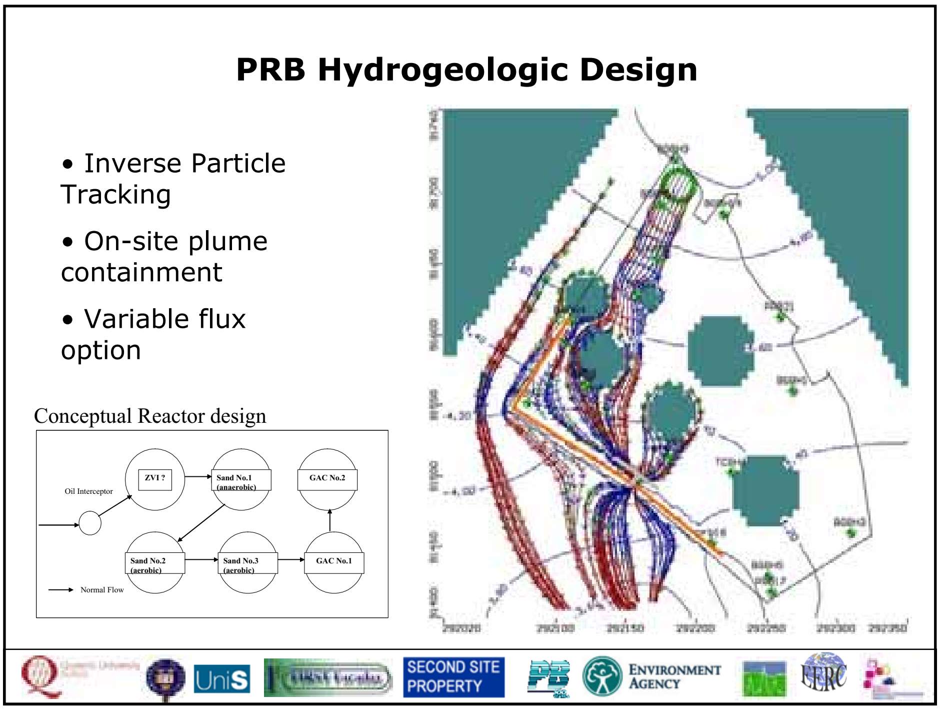
Model Calibration Process

- Complexity increased
- Addition of Heterogeneous hydraulic conductivities & gasholders
- Imported chemical data into MT3DMS
- Possible source areas identified (gasholder founds)



Model Calibration Process

- •Plume capture of contamination beyond site boundaries ?
- •A slurry wall of 10^{-9}m/s will eventually allow some contamination through



PRB Hydrogeologic Design

- • Inverse Particle Tracking
- • On-site plume containment
- • Variable flux option

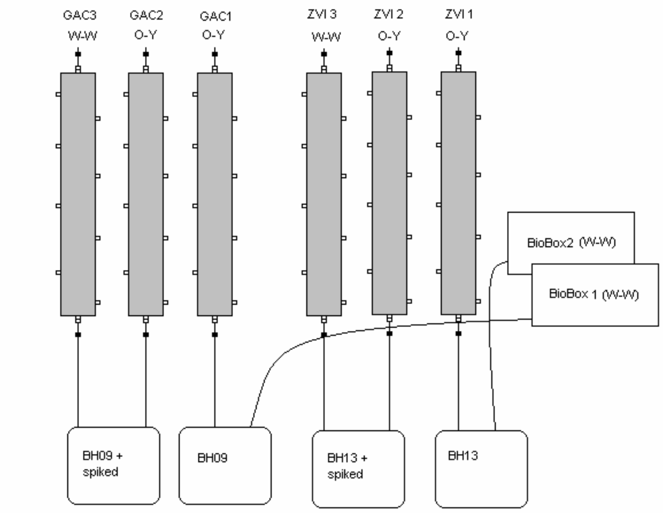
Conceptual Reactor design

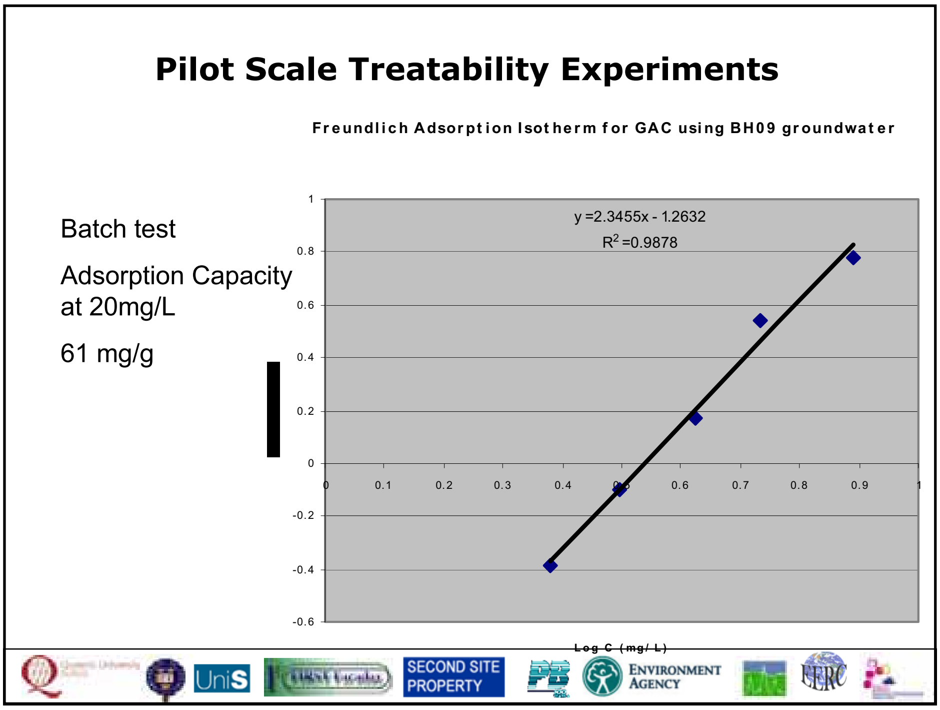
Pilot Scale Treatability Experiments

- **Batch tests**
- **Column tests**
- **Bioboxes**

- **All tests use contaminated groundwater from the Haven Road site**

Pilot Scale Treatability Experiments



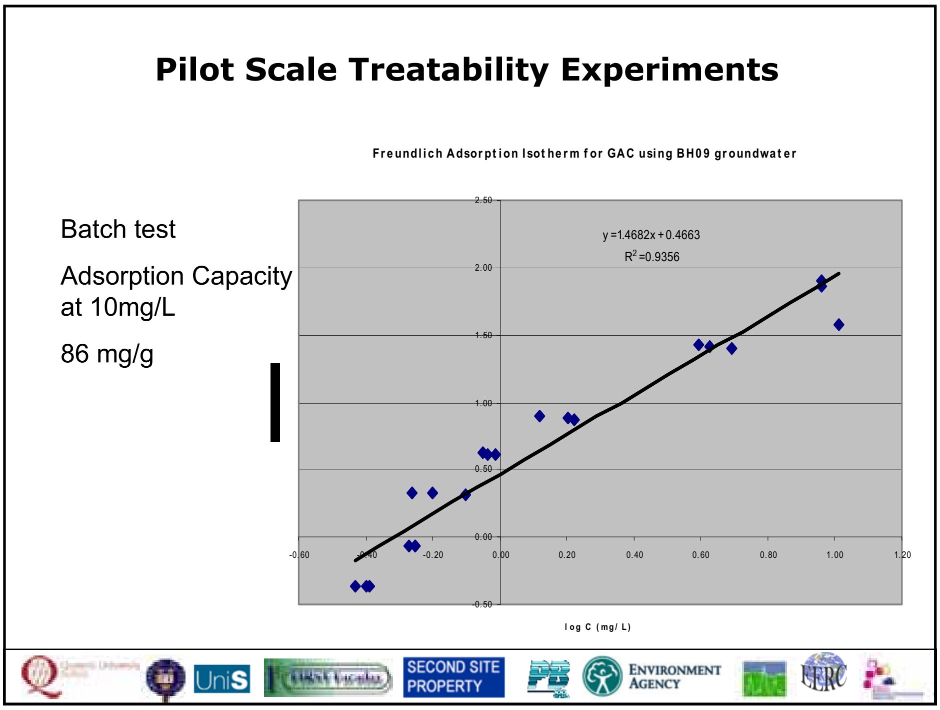


Pilot Scale Treatability Experiments

Batch test

Adsorption Capacity at 20mg/L

61 mg/g



Pilot Scale Treatability Experiments

Batch test

Adsorption Capacity at 10mg/L

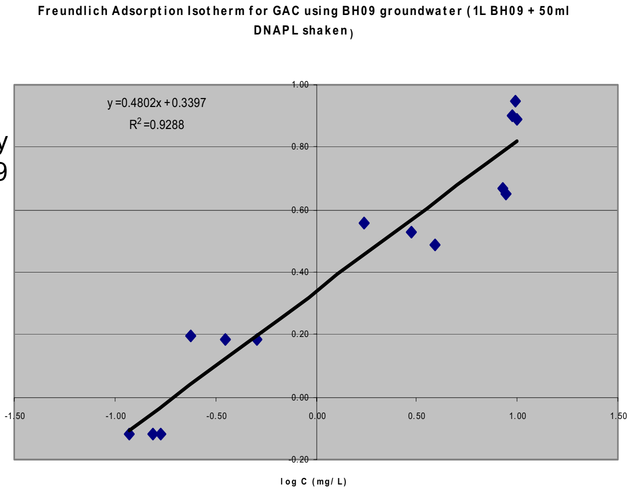
86 mg/g

Pilot Scale Treatability Experiments

Batch test

Adsorption Capacity at 20mg/L (1L BH09 + 50ml DNAPL shaken)

9.5 mg/g



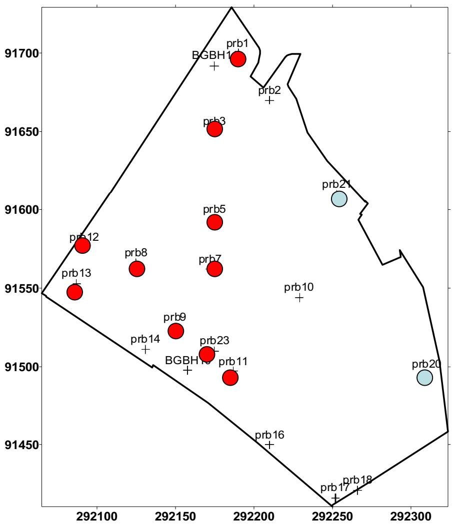
Microbial Research

- Soil core samples
  - Total plate counts
  - Utilization plate counts
  - Soil moisture content
  - Soil pH
  - MPN utilization counts
  - Toxicity testing
  - DNA isolation
  - Molecular community profiling
    - TGGE
    - DGGE (CEH)
- Groundwater samples
  - Total plate counts
  - Utilization plate counts
  - MPN utilization counts
  - Toxicity testing
  - DNA isolation
  - Molecular community profiling
    - TGGE
    - DGGE (CEH)

In-Situ Bioremediation of Cyanide, PAHs and Heterocyclic Compounds using Engineered SEquenced REactive BARrier (SEREBAR) Techniques

Robert Kalin

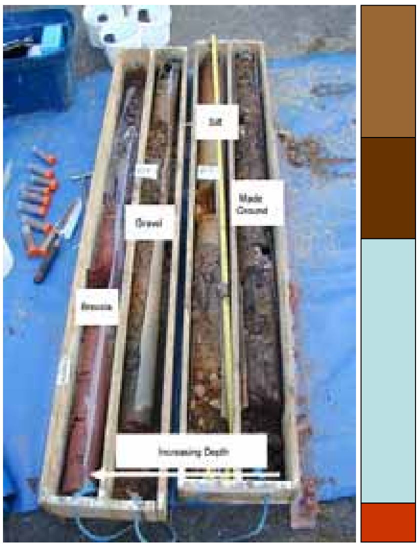
Sample Locations



● Contaminated areas Full microbial analysis

○ Uncontaminated areas (Control) Full microbial analysis

100 sample points



MG

Silt

Gravel

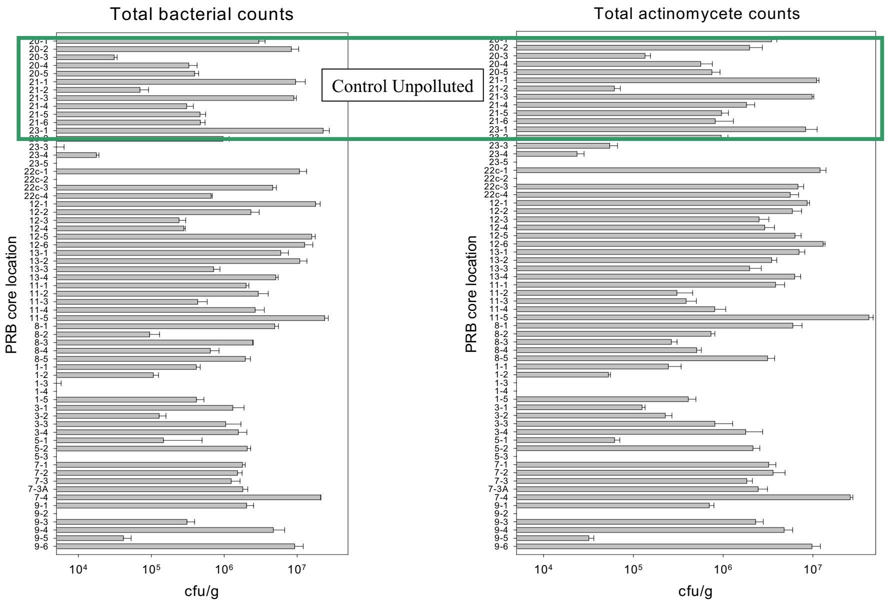
Breccia

Determined from lithology and contaminant load

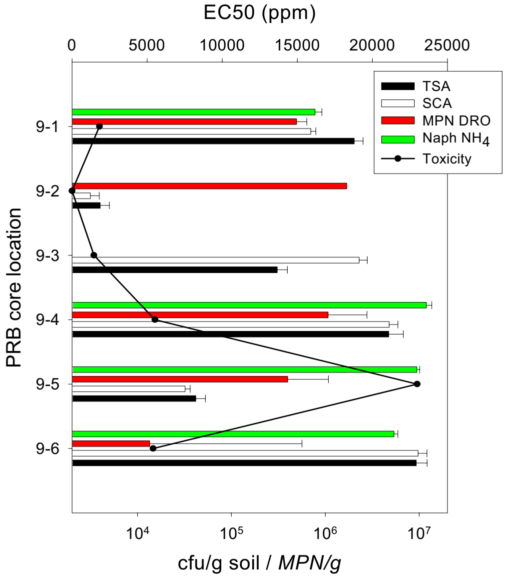
LNAPL

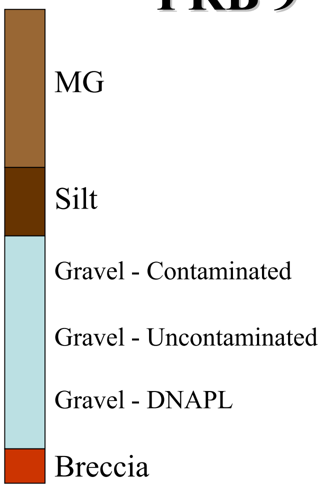
Dissolved phase

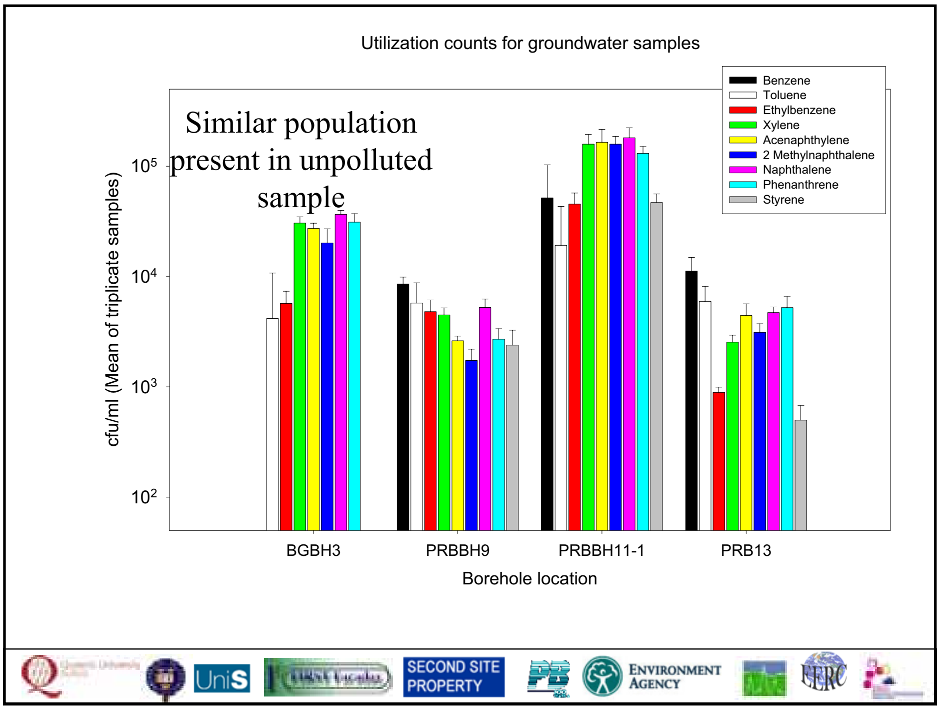
DNAPL


Total bacterial counts
Total actinomycete counts
Control Unpolluted
PRB core location
20-1
20-2
20-3
20-4
20-5
21-1
21-2
21-3
21-4
21-5
21-6
23-1
23-2
23-3
23-4
23-5
22c-1
22c-2
22c-3
22c-4
12-1
12-2
12-3
12-4
12-5
12-6
13-1
13-2
13-3
13-4
11-1
11-2
11-3
11-4
11-5
8-1
8-2
8-3
8-4
8-5
1-1
1-2
1-3
1-4
1-5
3-1
3-2
3-3
3-4
5-1
5-2
5-3
7-1
7-2
7-3
7-3A
7-4
9-1
9-2
9-3
9-4
9-5
9-6
10⁴
10⁵
10⁶
10⁷
cfu/g

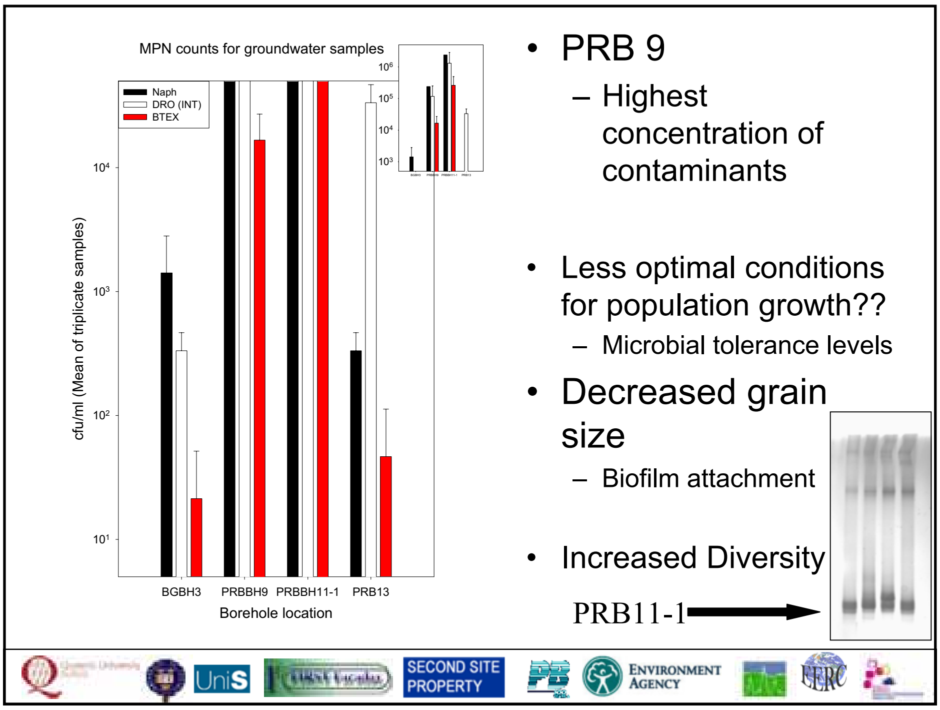
PRB 9


EC50 (ppm)
0
5000
10000
15000
20000
25000
TSA
SCA
MPN DRO
Naph NH4
Toxicity
PRB core location
9-1
9-2
9-3
9-4
9-5
9-6
10⁴
10⁵
10⁶
10⁷
cfu/g soil / MPN/g


MG
Silt
Gravel - Contaminated
Gravel - Uncontaminated
Gravel - DNAPL
Breccia

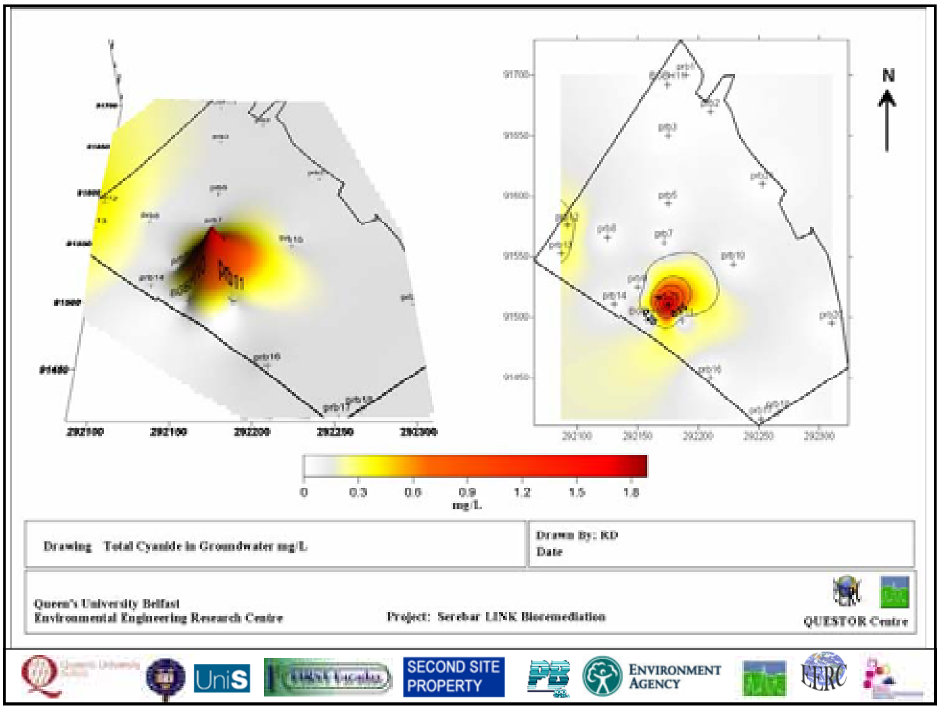


Similar population present in unpolluted sample



- PRB 9
  - Highest concentration of contaminants
- Less optimal conditions for population growth??
  - Microbial tolerance levels
- Decreased grain size
  - Biofilm attachment
- Increased Diversity

PRB11-1



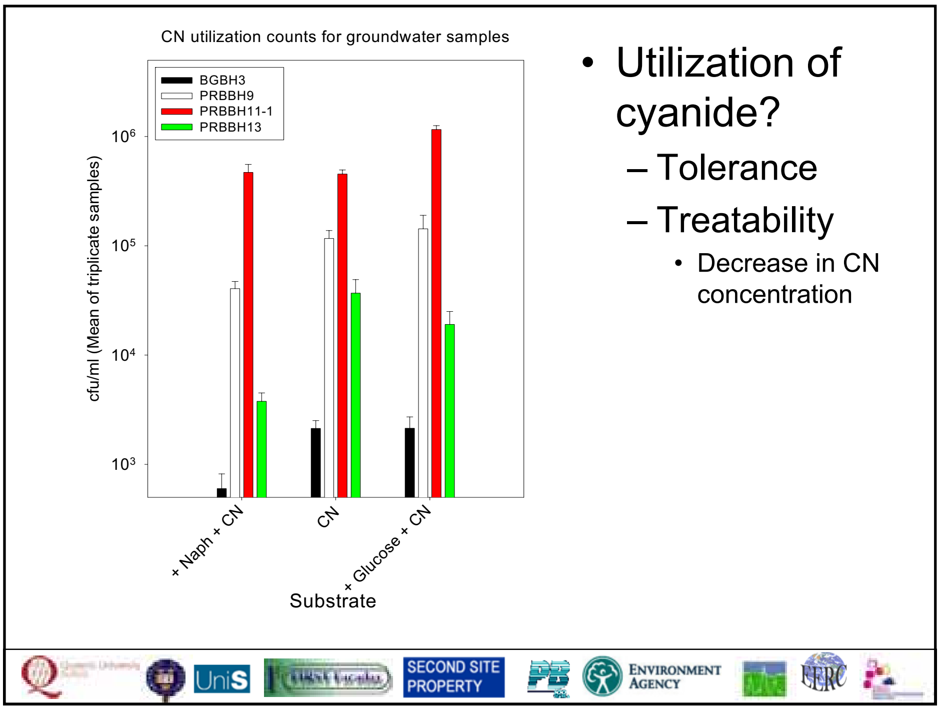
Drawing Total Cyanide in Groundwater mg/L

Drawn By: KD
Date

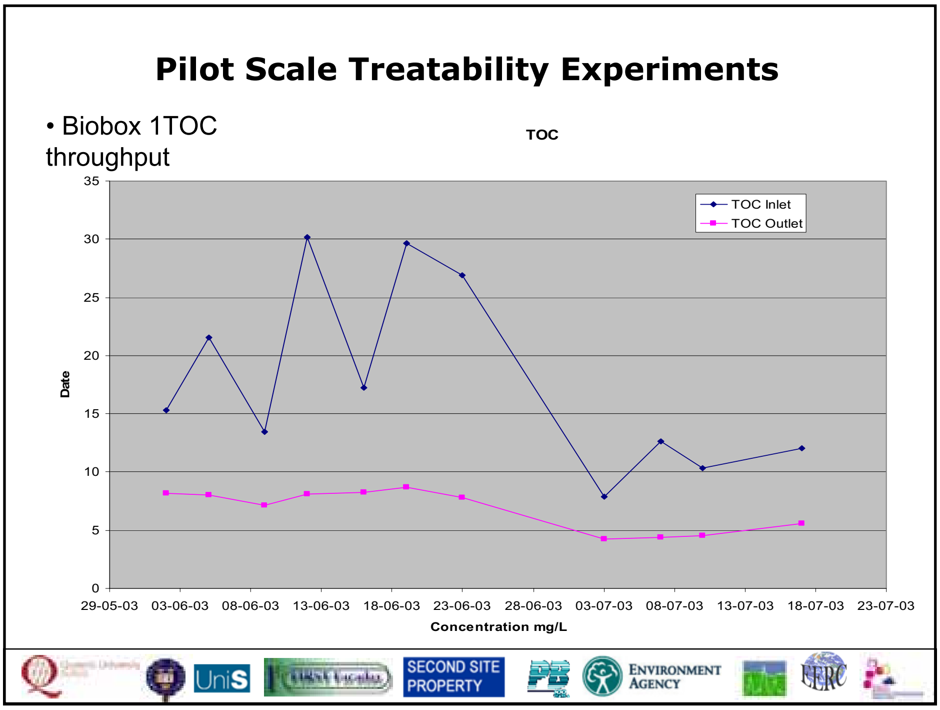
Queen's University Belfast
Environmental Engineering Research Centre

Project: Serebar LINK Bioremediation

QUESTOR Centre

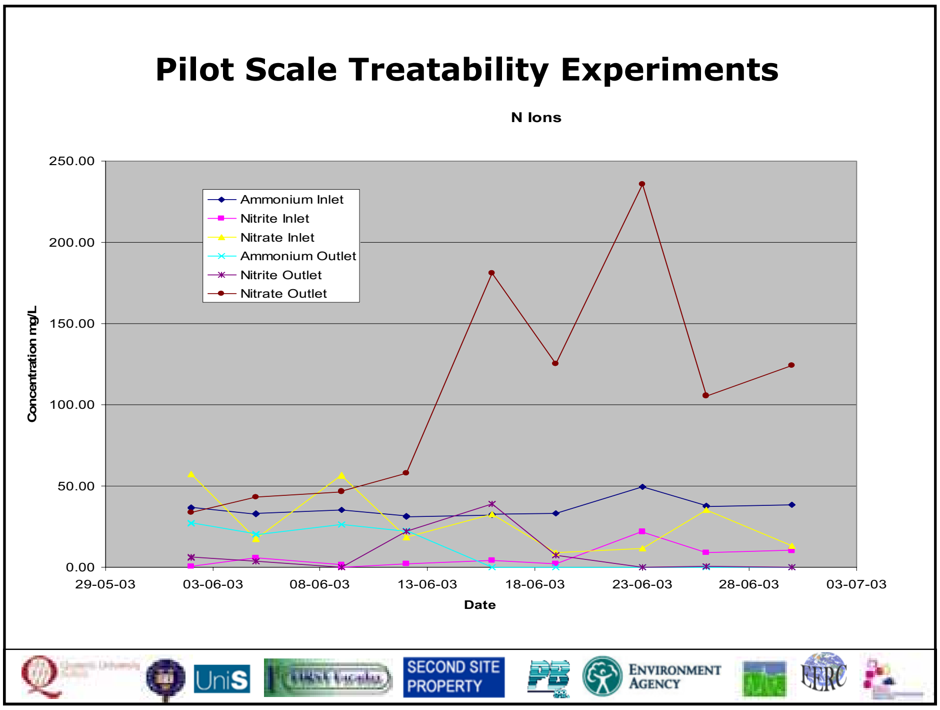


- Utilization of cyanide?
  - Tolerance
  - Treatability
    - Decrease in CN concentration



Pilot Scale Treatability Experiments

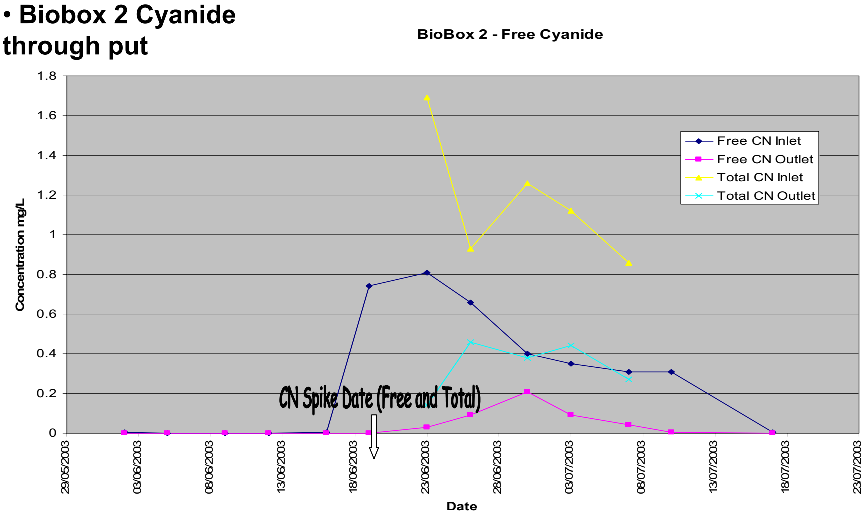
- Biobox 1TOC throughput



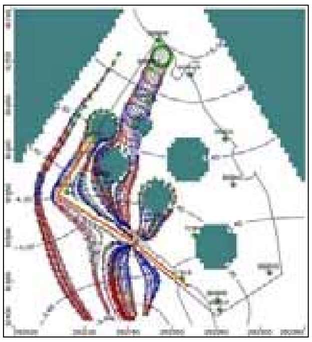
Pilot Scale Treatability Experiments

Pilot Scale Experiments

- **Biobox 2 Cyanide through put**

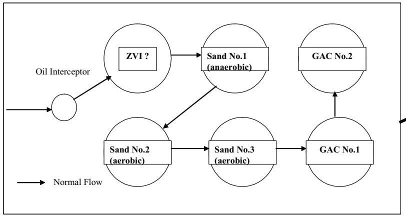


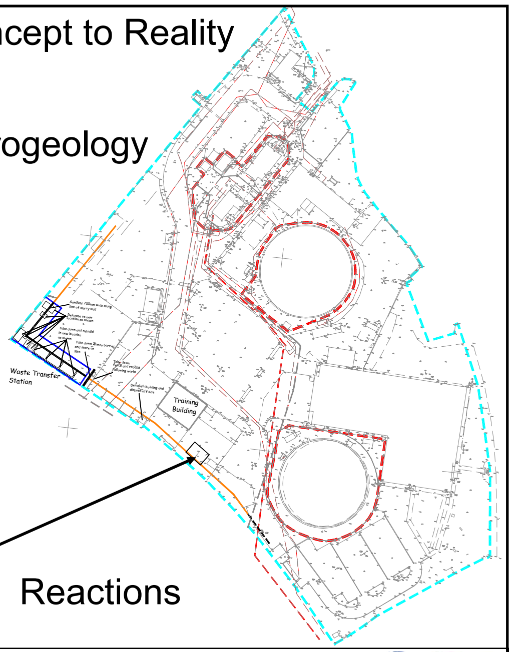
PRB Implementation: Concept to Reality



Hydrogeology

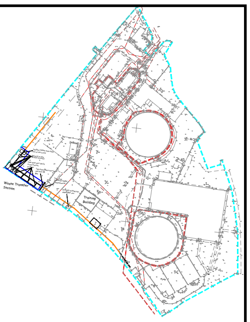
Conceptual Reactor design





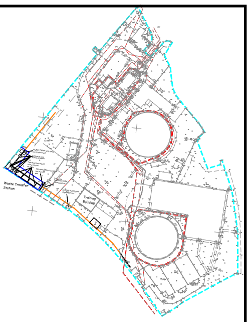
Reactions

PRB Implementation



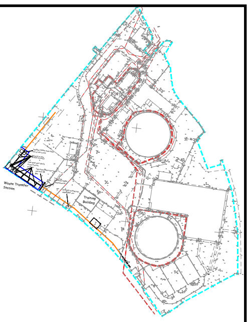
SPT
Gravels

PRB Implementation



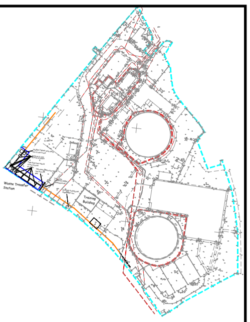
Slurry Wall

PRB Implementation



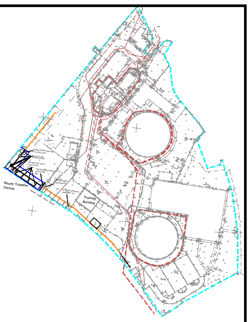
Slurry Wall

PRB Implementation



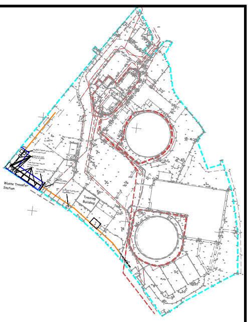
Slurry Wall
Installation

PRB Implementation



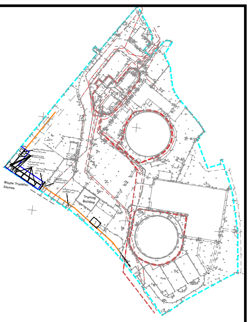
Services Crossing

PRB Implementation



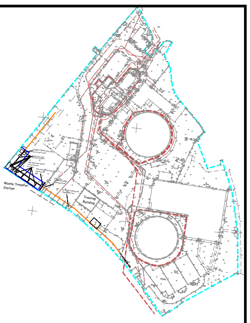
Pre-dig Slurry Wall

PRB Implementation

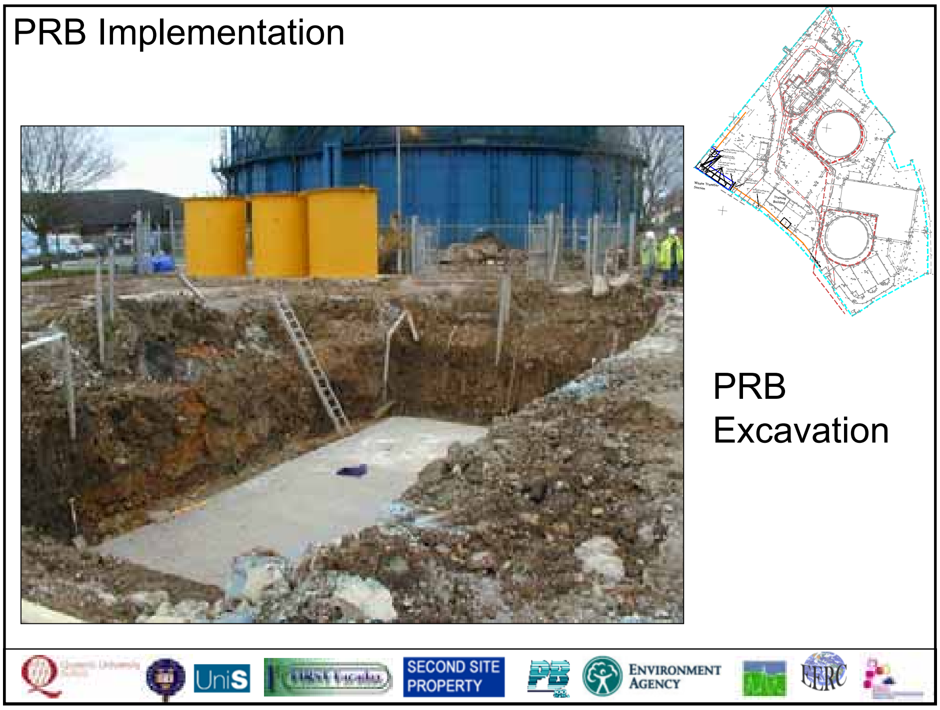


Gas-main Crossing

PRB Implementation

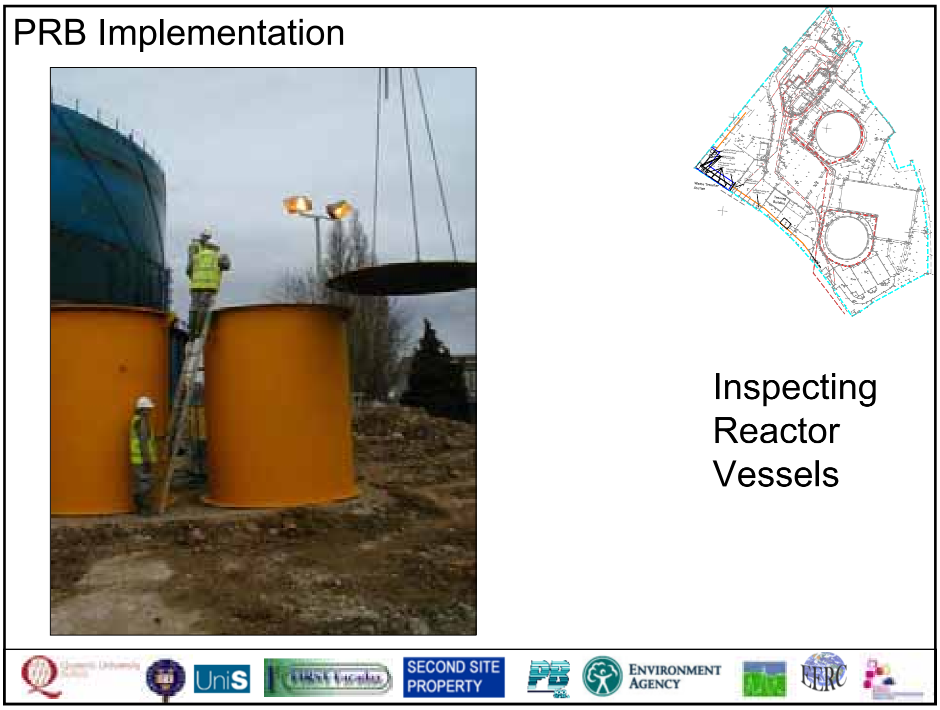


Layout PRB



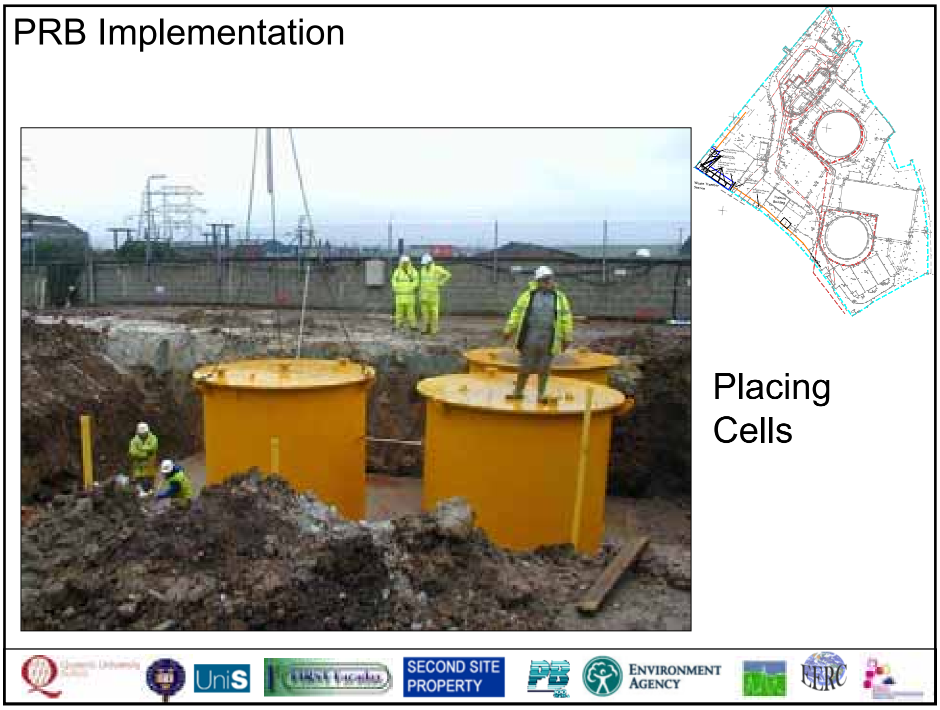
PRB Implementation

PRB Excavation



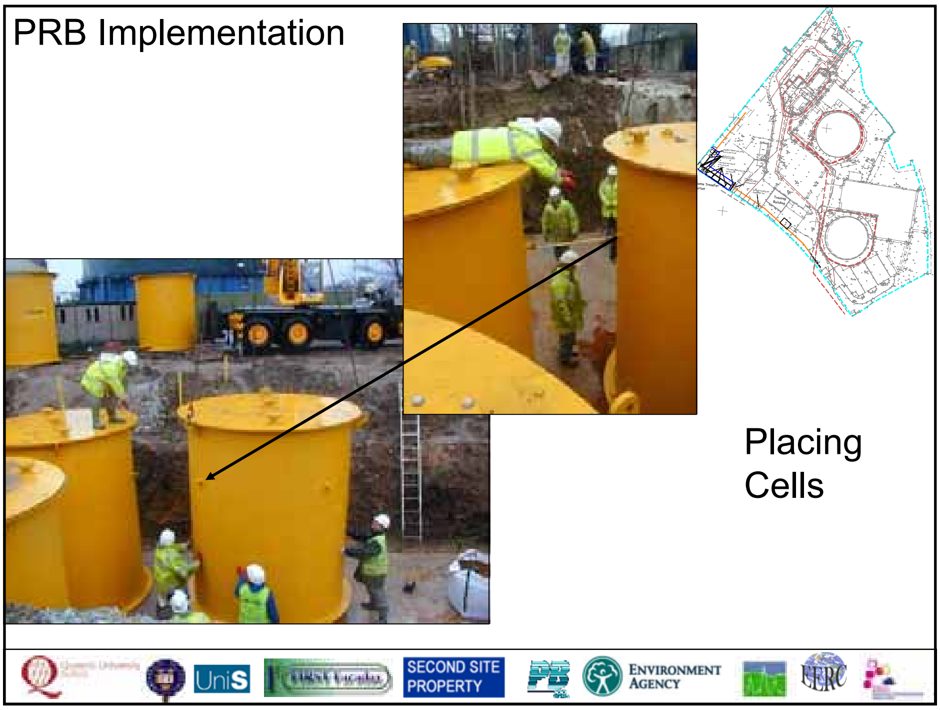
PRB Implementation

Inspecting Reactor Vessels



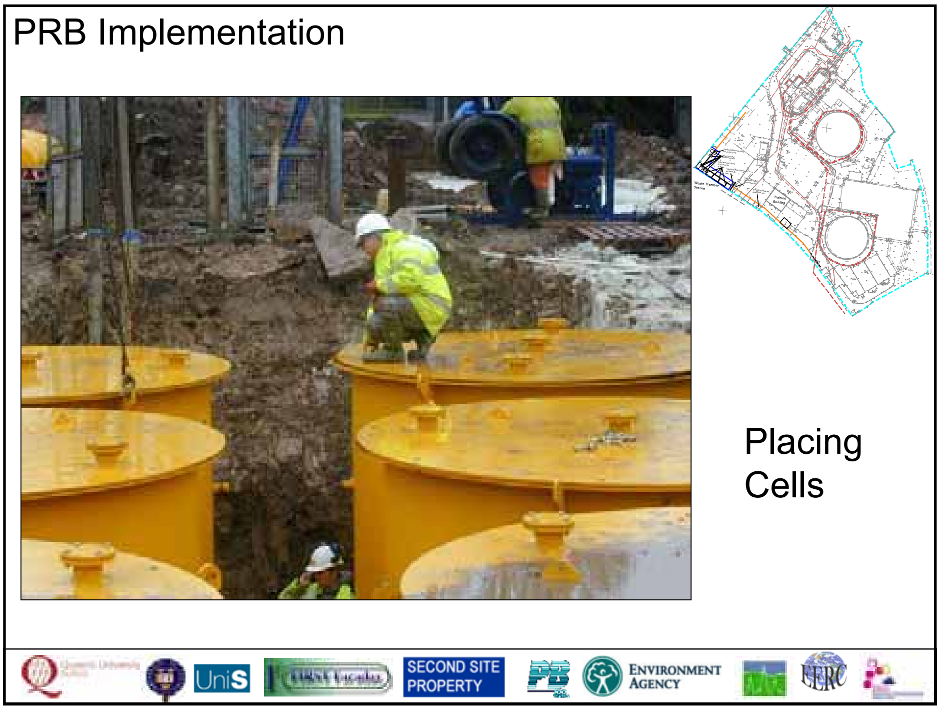
PRB Implementation

Placing Cells



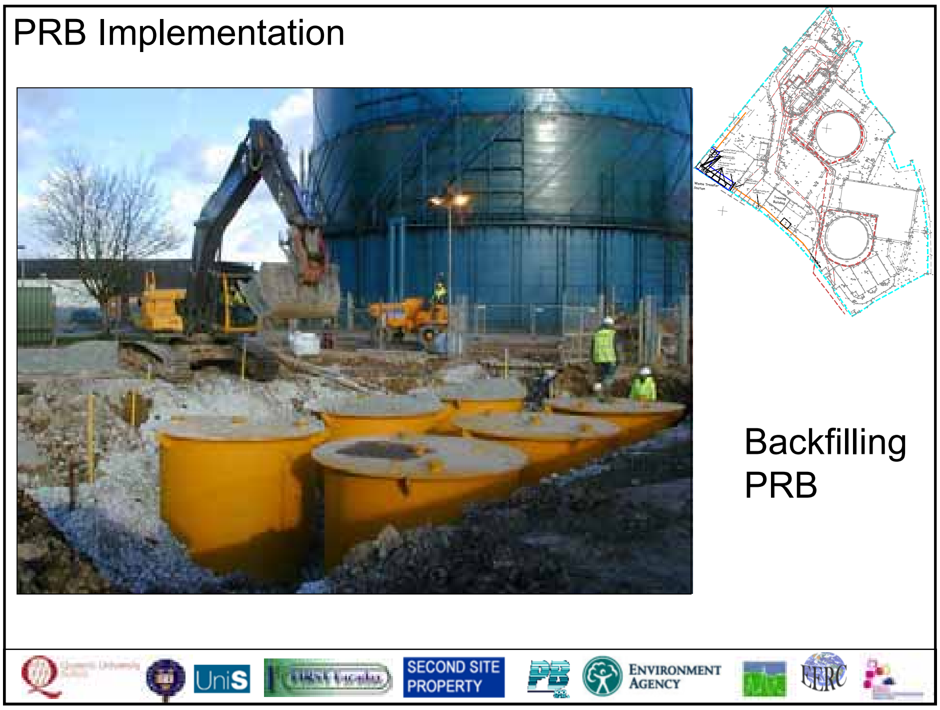
PRB Implementation

Placing Cells



PRB Implementation

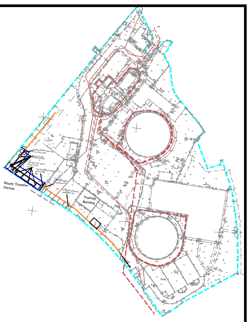
Placing Cells



PRB Implementation

Backfilling PRB

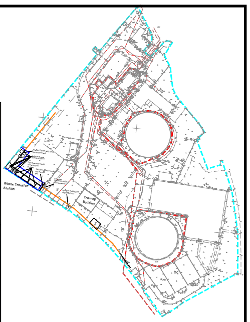
PRB Implementation



Inside
Reactor

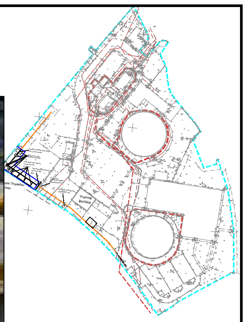
Weir inlet

PRB Implementation



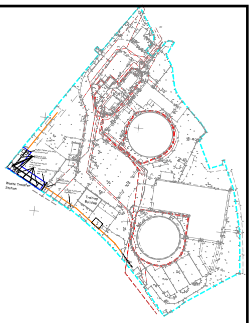
GAC
Cell

PRB Implementation



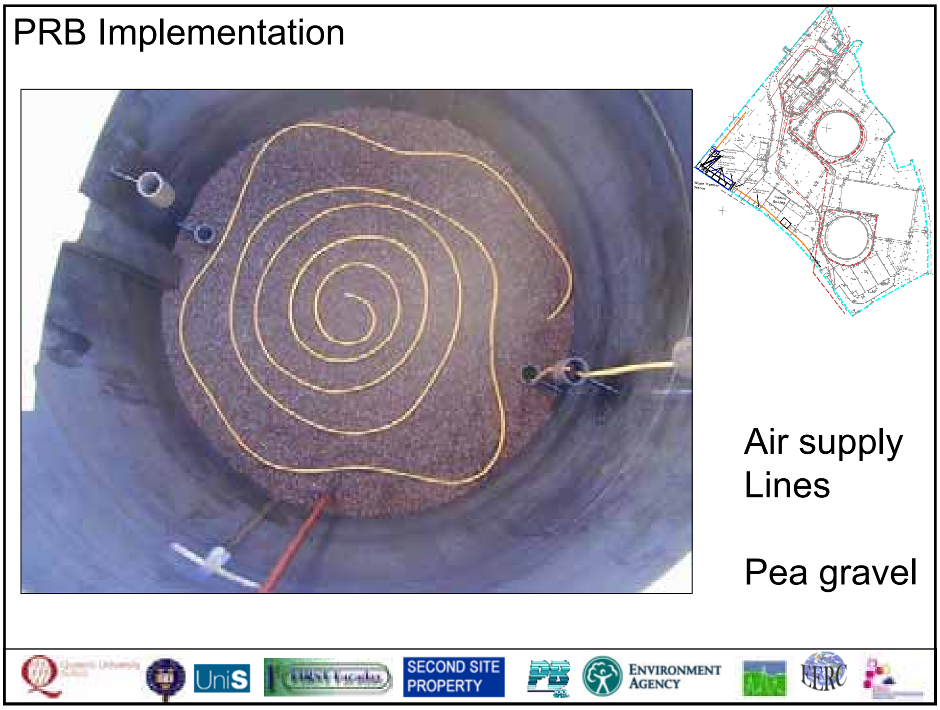
Filling GAC Cell

PRB Implementation



Inside Reactor

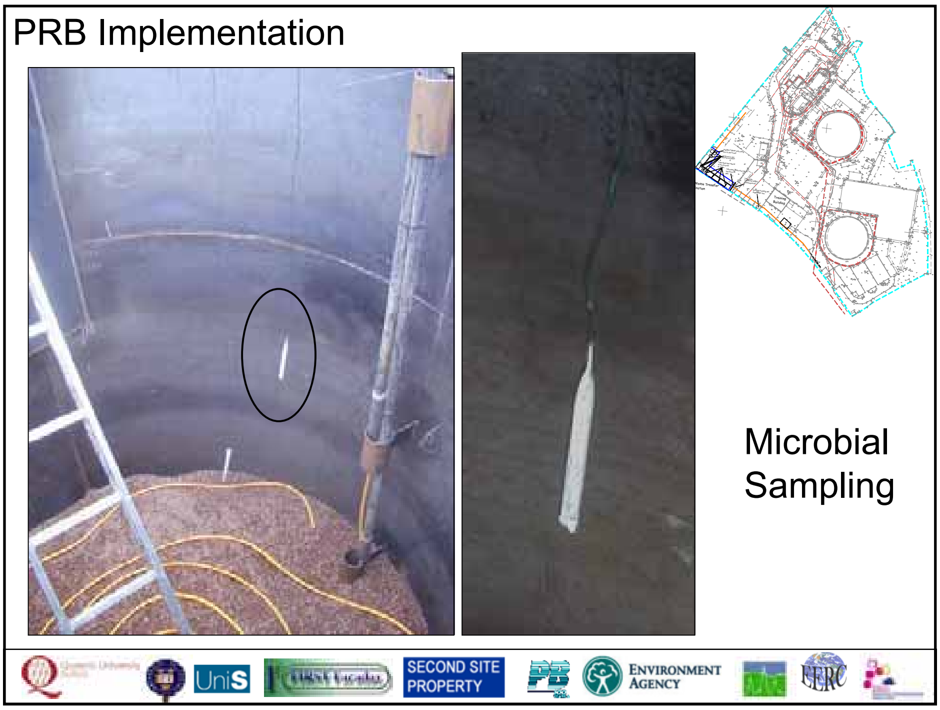
Exit collector



PRB Implementation

Air supply Lines

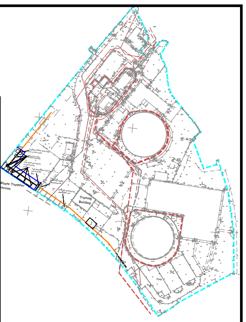
Pea gravel



PRB Implementation

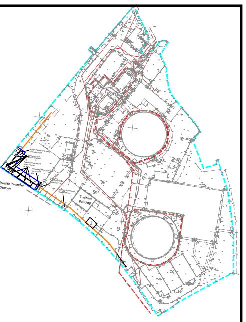
Microbial Sampling

PRB Implementation



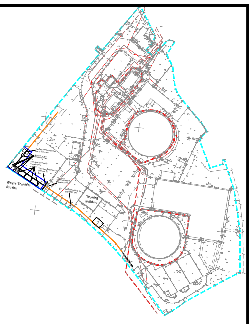
Sand into
Cells

PRB Implementation



Aerobic
Reactor

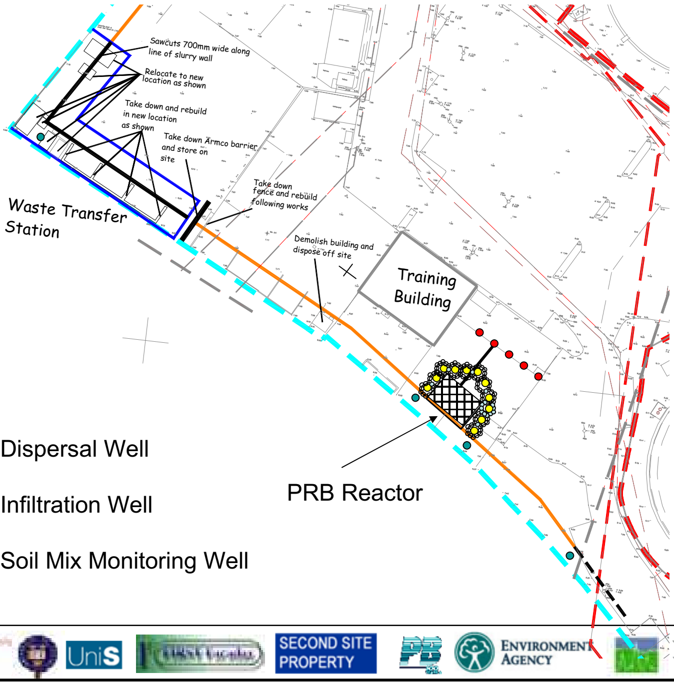
PRB Implementation



1. Set head-loss / weir adjust
2. Check telemetry
3. Check groundwater infiltration
4. Check
5. April 2004 commissioning

Monitoring monthly for SEREBAR Research

Evaluation and variation in the operation of Anaerobic / Aerobic / GAC sequenced reactive barrier system



● Dispersal Well

● Infiltration Well

○ Soil Mix Monitoring Well

PRB Reactor

Thank you &
QUESTION Time

r.kalin@qub.ac.uk

In-Situ Bioremediation of Cyanide, PAHs and Organic Compounds using Engineered SEquenced REactive BARrier (SEREBAR) Techniques: A Progress Report 0 to 14 months

Academic Partners
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Keith Dickson, Karen McGeough (Environmental Engineering Research Centre)
Dr. Mike Larkin, Dr. Andy Ferguson (QUESTOR Centre)
The Queen's University of Belfast (Lead Academic); Research Provider – Engineering and Microbiology

Prof. Chris Knowles, Prof. Mark Bailey, Dr. Wei Huang, Dr. Ian Thompson, Dr. Simon Jackman
Oxford Centre for Environmental Biotechnology & FIRSTFARADAY; Research Provider - Microbiology

Prof. Stephan Jefferis, Dr. Norman Kirkby, Dr. Ruben Rodriquez-Quintero
The University of Surrey; Research Provider – Design & GAC Modelling

Industrial Partners
Dr. Steve Wallace, Dr. Paddy Daly
Second-Site Property Holdings Ltd (Lead Industrial); Site Availability / IPMC

Jamie Robinson, Dr. Russell Thomas
Parsons Brinckerhoff; Consultant Technology Transfer

Regulatory Partner
Dr. Brian Bone
Environment Agency

Scientific Problem Addressed by TDP17

Brownfield sites and former/active industrial sites, including former coal gasification sites, often have recalcitrant contamination that is often neither easily nor effectively remediated *in-situ* to appropriate standards using active remediation techniques (pump-and-treat, source oxidation / sparging). World-wide, PRB technology is showing promise for remediation of groundwater plumes, including those associated with residual gas-works contamination including fuels and polycyclic aromatic hydrocarbons (PAHs) (EPSRC WPM project at Portadown see: http://www.prb-net.qub.ac.uk/eerg/dissemination/wpm/index.htm). Globally, Reactive Barrier Technology has been successfully implemented for treatment of chlorinated compounds (Belfast, UK and 'polishing' shallow ZVI wall in England), sorption of PAHs (Germany), and for the treatment of heavy metals (e.g. USEPA site in Elizabeth City, NC). Reactive Barrier Technology is proving to be a very attractive solution for problem holders, especially as a cost-effective means of managing risk at sites that have a moderate net value, where continued on-site activities dictate boundary interception of contaminants, and for which the costs associated with many treatment methods significantly exceeds the site's net value or for which the problem holder has limited financial resources available (as is the case for many residual brownfield sites in the UK that are awaiting remediation). These issues will continue to become more acute in the near future with the full implementation of the EC Landfill Directive (Council Directive 1999/31/EC).

In this project we proposed the expansion of Reactive Barrier Technology to include Sequential Treatment Steps that may be combined with either active or passive hydrogeologic control of groundwater. The researchers involved with this BBSRC Link proposal feel strongly that this approach, hereafter termed **Se**quential **Re**active **Bar**rier (SEREBAR) Techniques, can provide a potential break-through for solving problems in contaminated land and groundwater remediation akin to the impact that the introduction and application of wastewater treatment plants provided to the water resource industry. In fact, the concepts are not dissimilar, but SEREBAR Techniques require consideration within a risk-based framework that involves long residence times associated with natural groundwater movement coupled with innovative passive treatment solutions.

To realize the full potential of SEREBAR technology in the UK there is a need to combine novel scientific understanding of biodegradative potential and mechanisms with engineering tools that can predict long-term performance of SEREBAR technology. To date, there is no full-scale implementation of Sequenced Biologic Reactive Barrier Technology in the United Kingdom and globally, this approach is at very early stages of application.

Additionally, there is a need to focus R&D activities such as those in the CL:AIRE TDP17 / BBSRC Link programme not only on the interface of bioremediation and engineering science, but also on those classes or mixed classes of contaminants that are ‘harder’ to bioremediate. Though considerable research has been carried out on the biodegradation of cyanides, PAHs and heterocyclic compounds, much less is known about the *in-situ* degradation (or formation) and contaminant treatment (engineering), and potential fate / transport / risk issues associated with unknown compounds that might form during engineered biodegradation. Thus, because these compounds (heterocyclic) are an emerging class of contaminants and will be of particular concern throughout Europe when considered within the Source-Pathway-Receptor framework. This project will evaluate not only the degradation of priority pollutants known to exist at the field site near Devon, but will also study the formation and degradation of metabolites that may be of importance as future compounds of concern.

Scientific Research Solution

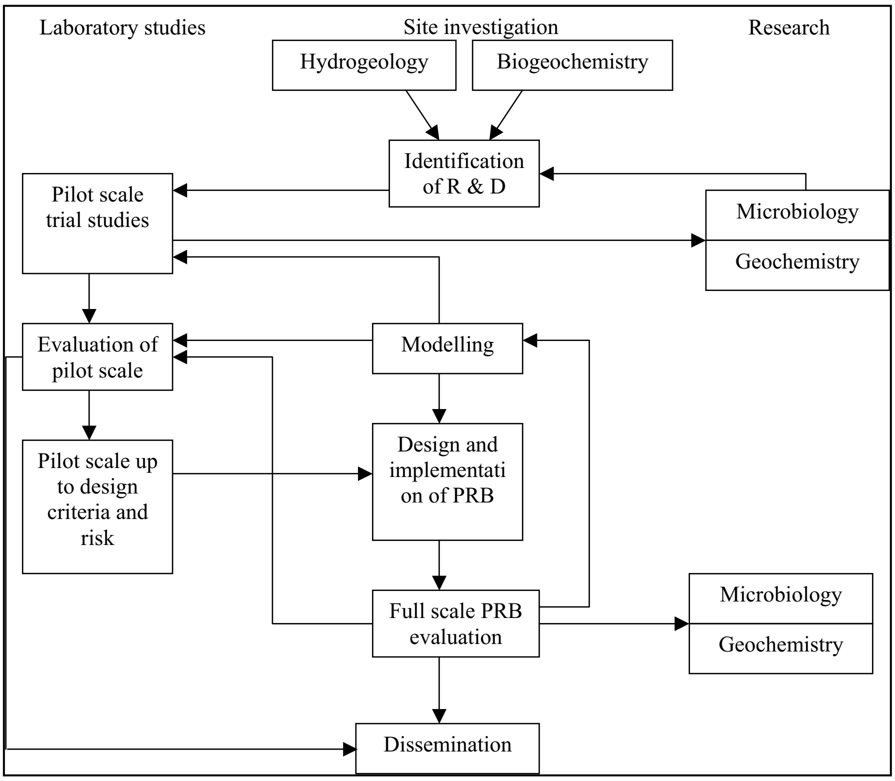
Bioremediation with SEREBAR Technology is likely a significant scientific and engineering challenge. The complete degradation of man-made or xenobiotic chemicals by microorganisms in the environment is universally considered to be beneficial. In particular the PAHs and cyanide (free or metal complexed) are of particular concern as high priority pollutants of soils and groundwater’s with regard to carcinogenicity and toxicity (EU Council Directive 2000/60/EC). The concept of "microbial infallibility" with respect to biodegradation has long been the assumption. Indeed, Stanley Dagley concluded in his introduction to the text "*Microbial Degradation of Organic Compounds*" that "On thermodynamic grounds, no organic compound can be excluded from serving as a possible energy source for aerobic microorganisms".

The research is expected to show that a permeable reactive bioreactor can be sequenced to degrade complex mixtures of contaminants such as organics (including PAHs, phenolics, creosols, BTEX, etc) and cyanides. This will require SEREBAR techniques that include the following features *:*

- Creation of effective aerobic and anaerobic zones for contaminant degradation and an understanding of the microbial processes therein
- Avoidance of clogging by inorganic precipitates e.g. carbonate, metal complexes / oxihydroxides
- Minimising biofilm fouling to maintain effective flow characteristics.

Aim of Research Project & Advancement to the State-of-the-Art

Innovation is required in the bioremediation market to continually provide cost-effective and ‘time-efficient’ (within risk framework time effective may be decades) remedial technologies. Reactive Barrier Technology has been implemented in ca. 95 sites worldwide (statistics from PRB-Net meeting, QUB March 2004). This is an extremely insignificant implementation of the technology on the global scale when compared with pump-and-treat and dig-and-dump! The main barrier to implementation is the lack of confidence in the technology, and to the range of problems associated with the technology (e.g. the vast majority of those installations are related to ZVI treatment of CHCs). Sequenced Reactive Barrier methods are in their infancy on the world market, and support for this project would provide technology providers in the UK with a global market advantage by the provision of a full-scale demonstration of the technology backed up by a detailed scientific and engineering understanding of the technology. This project is innovative, not only in the SEREBAR approach, but also in the class of contaminants that are to be treated.



The aim of this CL:AIRE TDP 17 / BBSRC-Link project is to demonstrate a full-scale implementation, from the laboratory to the field scale, of a SEREBAR biologic reactive barrier. This project will provide to UK Plc. a full-scale demonstration of the feasibility and application of Reactive Barrier Technology within a risk-based framework for land and groundwater contaminated with coal carbonization by-products through the severing of the Source-Pathway-Receptor chain.

Beyond the 1500 or so former coal gasification sites that still require remediation in the UK, knowledge of the treatment of cyanides will be of benefit to the mining industry, the knowledge of treatment for PAHs will benefit those sites with concurrent PAH contamination with mineral oils and DRO, and a better understanding of the interface between process engineering and science for SEREBAR PRB technology will provide a significant step forward in a more general up-take of this technology resulting in a market advantage for UK companies.

The general deliverable items for this project are to:

1) Install a working SEREBAR system on a Second-Site Property site, which would act as an effective remediation solution and also act as a flagship site in the UK for companies interested in sequential treatment trains within permeable bioactive barrier technology.
2) Undertake a high quality research project investigating all the variables associated with installing a SEREBAR system on a former gasworks in GB.
3) Provide an assessment of the effectiveness of both aerobic and anaerobic bioactive SEREBAR systems to degrade the target compounds and define the key physiological parameters under both conditions. Understand the fundamental microbial problems associated with pollutant hydrocarbon and cyanide degradation in the PRB.
4) Develop modeling tools for design and predictive evaluation of SEREBAR performance.
5) Increase the understanding and knowledge of PRBs and SEREBAR Technology for implementation and market exploitation.

Objectives of the project are:

1) To sufficiently characterize a site so that the installation of an SEREBAR reactive barrier system will effectively manage risk at a former coal gasification Southwest England, UK. This will include biogeochemical analysis and groundwater modeling (Prof Kalin's group at QUB for chemical analysis with PB).
2) To identify and characterize the physiological limitations of the key microorganisms involved in the biodegradation of target compounds under aerobic and anaerobic conditions, and determine the main chemical limitations to effective biodegradation. This will include *in situ* assessment of the bioreactor. Research at Belfast will concentrate aerobic bioremediation of BTEX, PAH's and heterocyclic compounds whilst Oxford will focus on cyanide bioremediation including microbial community dynamics. Research at Surrey will concentrate on modeling of the interface between chemical and civil engineering.
3) To test samples of contaminated groundwater for treatability using both aerobic and anaerobic SEREBAR systems at both lab and pilot scale. This will largely take place in Belfast with microbial community studies and cyanide removal aspects handled at Oxford.
4) To build a full-scale SEREBAR reactor on a site in Southwest England, UK.
5) To monitor the performance of the SEREBAR system including analysis using molecular ecology techniques of the microbial populations that mediate biodegradation, study of suitable conditions to be maintained within the barrier for sustainable biodegradation to occur, and evaluating/modeling the risks of biofilm formation and its effect on barrier performance;
6) To design both short term (first year or period of project) and long term monitoring programmes (period to necessary for removing the risks). The latter may be aided by the use of those modeling tools developed within the BBSRC Link project as suitable for indicating long-term performance of these systems.

Site Selection

The SEREBAR field site was selected such that the installation of the PRB provided a risk-management solution during on-going operational activities. The ethos of the research project was to provide a solution where none previously existed, and the PRB is the only viable option to deal with dissolved contaminants in a groundwater plume beneath existing structures that remain operational.

Figure 1 & 1a: Site selection in the Southwest of England. The site is currently active and used for gas distribution. The PRB is used as a risk-management option during the on-going activities of the site without decommissioning of the current operations.

Progress Report: Site Investigation, Hydrogeology and Contaminant Transport

During the period February 2003 to May 2003 additional intrusive site investigation, groundwater sampling, geotechnical and hydrogeologic site investigation was undertaken. Adaptive sampling methods were used to up-date locations for monitoring / investigation boreholes to optimize the cost-benefit for the SI.

Figures 2a and 2b: The generalized geology of the site is shown where made ground overlies a silt, which in turn overlies and marginally confines the main gravel aquifer that is underlain by weathered breccia (the main hard-rock geologic unit in the area).

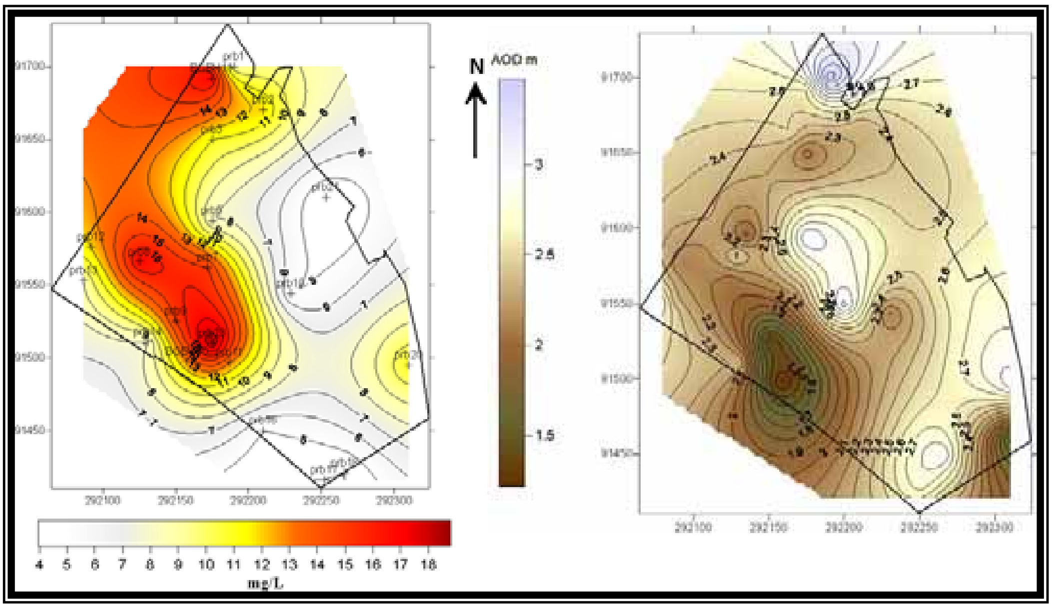


Figure 3: The contaminant transport (as represented by a TOC plume shown in the left of Figure 3) at the site is strongly controlled by the base of the gravel aquifer (as shown in the topographic map in the right of Figure 3). The gravel aquifer is generally 2 to 3 meters in thickness across the site and therefore does not represent a major regional source of water.

Progress Report: Conceptual Design, Construction, Implementation

Site groundwater was collected and transported to the Queen's University of Belfast where treatability studies were undertaken over a 9 month period of time. The results of these studies were used to determine the rate of biologic degradation, study of microbial activity and ecology, and the affect of design variable on the effective degradation / removal of contaminants from groundwater.

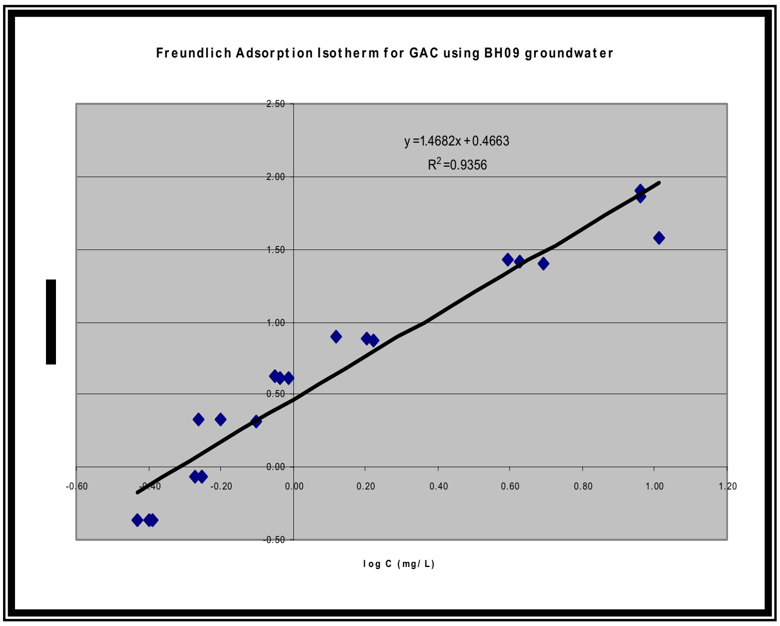
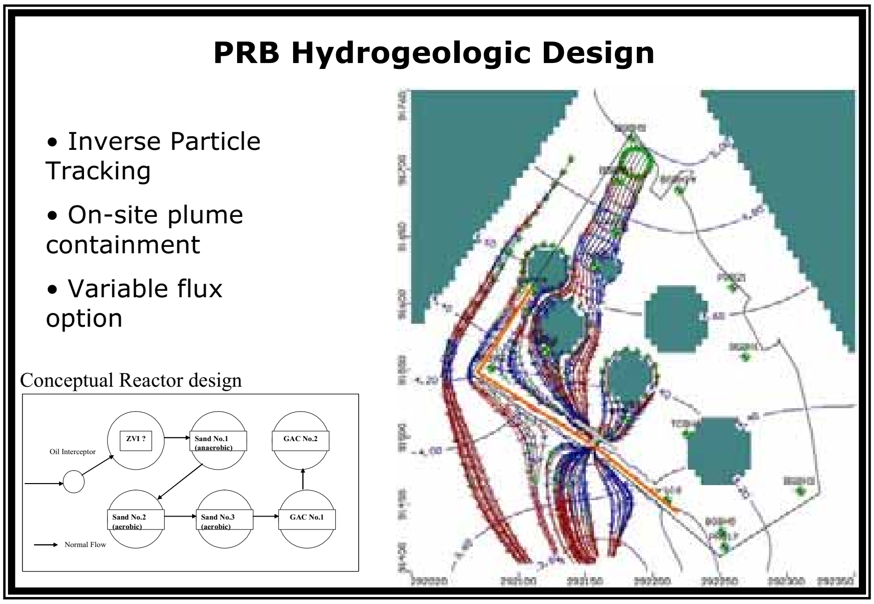


Figure 4: A representative series of data for sorption using GAC for site groundwater.

Figure 4 shows a representative series of data for sorption using GAC for site groundwater. GAC is 'fail-safe' design parameter for the PRB should the long-term effectiveness of biologic activity vary, and it is a back-up during maintenance of the sequenced regions of the PRB.

The conceptual design included hydrogeologic evaluation for plume capture, a series of reactors that included potentially Zero Valent Iron, Anaerobic biodegradation, Aerobic Biodegradation and GAC.



PRB Hydrogeologic Design

- Inverse Particle Tracking
- On-site plume containment
- Variable flux option

Figure 5: Hydrogeologic design of the PRB.

Between August 2003 and October 2003 tender documents were prepared that outlined the design requirements of flux and expected residence times (with significant factors of safety). Competitive tendering was completed in early December 2003 and an approved contractor chosen. Final designs were approved in January 2004.

Progress Report: Construction

Construction is on-going and expected completion and validation of operation is expected mid- to late- April 2004. Operational details and monitoring results will be provided in future CL:AIRE / BBSRC Link dissemination events as well as in reports.

Figure 6: Construction of the PRB.

At the time of this CL:AIRE conference, this project is still on-going and all information in this paper and presented at the conference will be revised upon completion and publication of TDP17 CL:AIRE report.

Biographical Note

Dr. Andy Cundy

Dr. Andy Cundy is an environmental geochemist at the University of Sussex, who specialises in the environmental behaviour of radionuclides and heavy metals, and the interaction of contaminants with sediments and rocks. After his first degree in ocean sciences at the University of Plymouth, he undertook a PhD at the University of Southampton investigating radionuclide and heavy metal contamination along the south coast of England. Following his PhD, he has spent 10 years lecturing at 3 U.K. universities, and has worked on environmental geochemistry in four continents in projects funded by government, the Atomic Weapons Establishment, Environment Agency, EU and private industry. In his spare time, he practices and teaches karate.

Dr. Laurence Hopkinson

Dr. Laurence Hopkinson is a mineralogist/applied geologist at the University of Brighton, who specialises in solid-solution chemistry, mineral formation and applications of geochemistry to civil engineering. After a first degree in geology at the University of Greenwich, he undertook a PhD at the University of Southampton investigating ocean crust mineralization. Following his PhD, he has spent 10 years researching and teaching at 2 U.K. and 1 overseas universities, and has worked on the mineralogy/geochemistry of a range of mineralising geological systems, in projects funded by government (NERC), universities, armed forces and private industry. In his spare time, he is a father to two young children.

Ferric Iron Remediation and Stabilisation (FIRS) – developing a new electrokinetic remediation technique for heavy metal- and As-contaminated sites.

Andy Cundy[1] and Laurence Hopkinson[2]

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Plan:

Introduction: Electrokinetic remediation

The FIRS technique: rationale and data from bench-scale studies

Towards a field-based technique: CL:AIRE project RP15

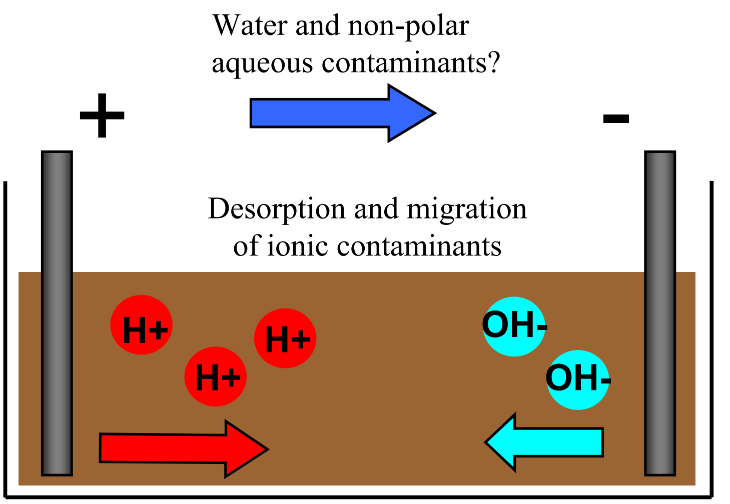
Conclusions

Introduction

Although clays and silts at contaminated sites tend to sequester large quantities of heavy metals, radionuclides, and selected organic pollutants, they are relatively resistant to remediation with traditional technologies (e.g. pump and treat, soil washing) because of their low hydraulic conductivities.

This has stimulated a considerable amount of research into cost-effective, in-situ techniques that can be used to remediate low-permeability, high clay content soils.

One emerging technology that has received much attention is electrokinetic remediation. Electrokinetics is a process that separates and extracts organic, inorganic, and radioactive contaminants from saturated or unsaturated clay-rich soils, sludges and sediments under the influence of an applied electrical field.



$H_2O \rightarrow 2H^+ + 1/2\ O_2$ (gas) + $2e^-$

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (gas)

Despite promising experimental results, however, at present there is no standardised universal electrokinetic soil/sediment remediation approach. Instead there are a number of technologies (e.g., Lasagna™, Electro-Klean™, electrochemical geooxidation), each of which has different strengths, drawbacks, and operational and design requirements.

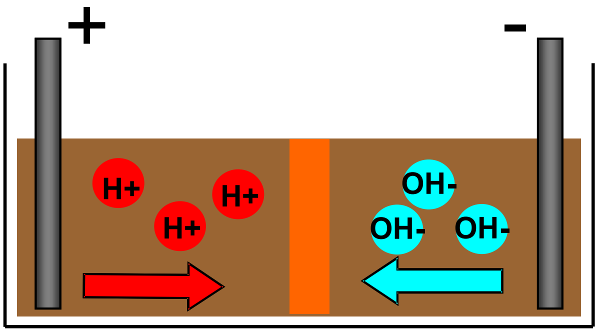
Many of the current technologies are technically complex and energy intensive, and geared towards the removal of 90% or more of specific contaminants, under very specific field or laboratory-based conditions.

However, in the real environment a low-tech, low-energy contaminant reduction / containment technique may be more appropriate and realistic. Such a technique (FIRS) is discussed here.

The FIRS technique

The FIRS technique (Ferric Iron Remediation and Stabilisation) involves the application of a low magnitude (typically less than 0.2V/cm) direct electric potential between two or more sacrificial, iron-rich, electrodes emplaced either side of a contaminated soil or sediment.

The electric potential is used to generate a strong pH / Eh gradient within the soil column, and force the precipitation of an iron-rich (sorptive) barrier in the soil between the electrodes at the boundary between the acid and alkaline “fronts”



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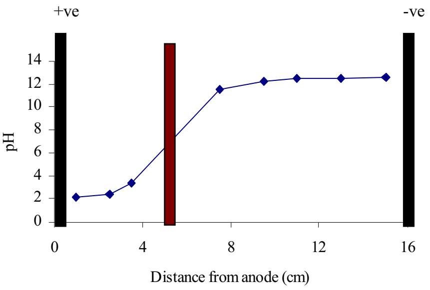
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (gas)

Ferric Iron Remediation and Stabilisation (FIRS) –
developing a new electrokinetic remediation technique for heavy metal- and As-contaminated sites

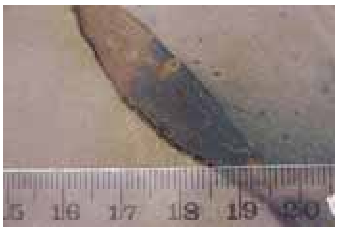
Andy Cundy and Laurence Hopkinson

The acid front “acid-washes” the soil, while the precipitated iron band provides an impermeable barrier to contaminant migration, and, together with the pH gradient, provides a chemical trap for a range of inorganic, organic and radioactive contaminants.......



pH gradient measured in radionuclide-contaminated mud, after 410 hours of application of a 1.5V potential difference, using a seawater electrolyte and electrode separation of 16.5cm

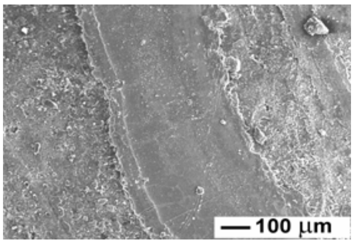
Sub-vertical, 1cm thick Fe-rich band generated in water-saturated sands after 30 hours application of a 1.5V potential difference between cast iron electrodes.



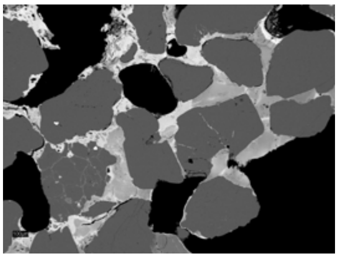
The system mimics natural mineralisation processes, where internal electric fields present in rock and soil bodies can generate multiple bands of ironstone via precipitation of iron oxides and hydroxides

In the FIRS technique, these iron-rich bands are grown over timescales of 3 – 400 hours, and consist of amorphous (or microcrystalline) iron “pans” (a), or, in sandy soils, a coating of goethite, magnetite and zero-valent iron? which cements mineral grains (b).

A



B



Results from a range of bench-top studies illustrate the potential of the FIRS technique for contaminated leachate confinement and contaminated land remediation:

(a) Hydrocarbon and Cu contaminated sediments, Southampton Water

Mud sample from Southampton Water, contaminated with Cu and hydrocarbons from the nearby Fawley oil refinery and local shipping, was treated at 2V, in a 3D cell using a rectangular electrode array.

After 16 days, the electrokinetic treatment resulted in a ~60% or greater reduction in Cu contamination.

Liquid organic-rich effluent was exuded from the sediment, and channelled and drained at *ca*. 10ml per day from the surface of the cathodic compartment.

Energy requirement for experiment was 10.9 kW/m^3. Compares favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g., 500kW/m^3 for 100% removal of metal contaminants.

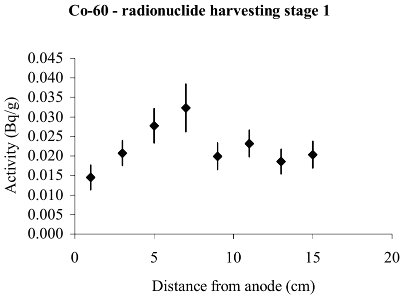
Time scale for copper decontamination of the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective membranes.

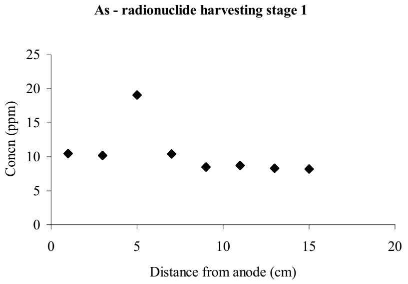
Use of cast iron electrodes (as opposed gold coated, platinum or graphite electrodes), means that the experimental system is low cost in terms of energy, materials and electrode construction, which typically make up ~70% of the costs associated with any electrokinetic remediation system.

(b) Radioactively-contaminated sediment, Ravenglass, Cumbria.

A clay-rich sediment sample, slightly contaminated with radionuclides, was collected from the Ravenglass estuary, Cumbria and treated at 1.5V for 410 hours in a 2D perspex cell. A 17mm thick Fe-rich band was generated 5cm from the anode, at the point where a major step in pH (from pH 2 to pH 13) occurred.

Geochemical and radiometric analysis of the treated sediment show clear removal of ^{60}Co from the anode zone of the cell, and precipitation of the remobilised ^{60}Co on, and in the cathode zone adjacent to, the iron-rich band. Notably, As, present as a trace contaminant in these sediments, was highly amenable to the FIRS treatment, with desorption occurring at high pHs in the cathode zone, and reprecipitation on the Fe-rich band.

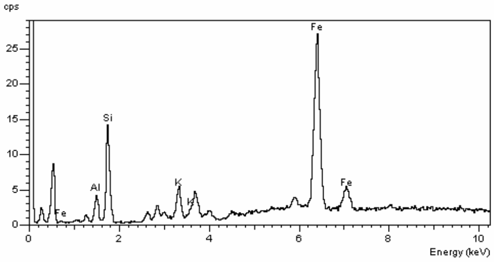


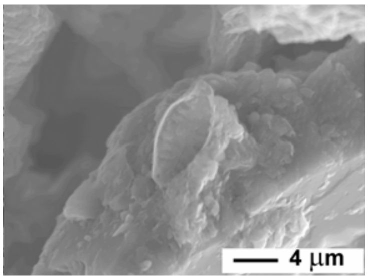


Geotechnical tests on the precipitated iron pan indicate a major loss of permeability following iron band formation - ~ 0.3 x 10^{-7} m/s (pre-treatment) vs. 10^{-9} m/s or less (i.e. effectively impermeable) in the precipitated iron band.

The approximate Uniaxial Compressive Strength of the iron band was 10.8N/mm^2 (comparable to, for example, a moderately lithified sandstone).

Large increase in shear strength in the anode zone sediment also observed following treatment, without any significant loss in porosity. SEM analysis of the treated anode zone sediments shows clear evidence for precipitation of iron oxides as a thin coating over mineral grains. These data therefore indicate that a significant improvement in the engineering properties of the anode zone sediments has occurred, probably as a consequence of cementation via precipitation of iron (and/or through electro-osmotic dewatering).

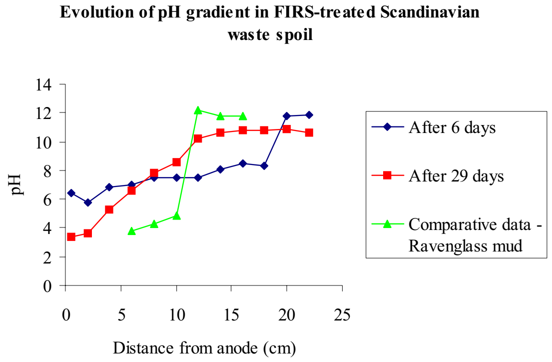




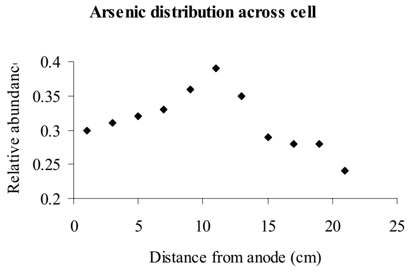
(c) Heavy metal contaminated waste spoil, Scandinavia.

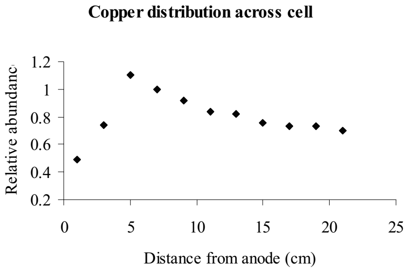
A hematite (iron-oxide)-rich waste spoil, contaminated with As, Cu, Pb and Zn, was collected from a former wood preservation site in Scandinavia, and treated for 29 days at 2V in a 3D Perspex cell.

A strong pH gradient developed relatively rapidly in the treated soil and became more pronounced over time, although a sharp pH jump of the type normally observed was not produced, presumably due to a buffering effect exerted by the soil.



Hence, a discrete, clearly-visible iron band did not form over the timescale of the experiment. BUT the continuous drop in pH and expansion of the acidic anode zone over the course of the experiment indicate that with longer treatment periods the precipitation of a distinct Fe-band would be induced. However, a highly alkaline zone and an acid zone were clearly generated in the cell, which caused significant remobilisation of As, Cu, Pb and Zn.





Hence, despite the heterogeneity and mineralogical characteristics of the spoil (which effectively make the contaminated material a "worst case scenario" in the application of electrokinetic techniques), the FIRS treatment has successfully caused a reduction in the concentration of a range of contaminants (albeit without the formation of a distinctive iron band),

TOWARDS A FIELD-BASED TECHNIQUE – CL:AIRE PROJECT RP15

The FIRS technique has significant potential for field-scale use, as it has already been successfully applied in decimetre-scale three-dimensional cells, and mimics a natural system that operates over scales in excess of 100 metres in geological systems.

The low voltage and current used mean that power requirements are likely to remain low even when the system is upscaled, and, coupled with the flexibility provided by the use of multiple, low cost electrodes, means that contaminated land can be sequentially treated with a series of electrode arrays, placed to avoid (or work around) site infrastructure, where the distance between individual electrodes does not exceed a few metres.

TOWARDS A FIELD-BASED TECHNIQUE – CL:AIRE PROJECT RP15

The recently approved CL:AIRE project RP15 will examine the use of the FIRS technique in remediating small working sites with relatively shallow contamination depth, as a first step in the development of the technique for field-scale use.

The primary aim of this research project is to develop the FIRS technology from prototype stage (i.e. bench-top scale) and test it at field scale – specifically at two heavy-metal contaminated, suburban garden sites in south Yorkshire. The project consists of two phases:

Phase 1 (field-scale laboratory trials), in which the existing FIRS system will be upscaled to treat metre-scale soil columns, and its remediation efficiency optimised for contaminated soil material from the proposed field-test sites;

Phase 2 (field trials), in which the FIRS system will be tested at two suburban garden sites (in south Yorkshire) which are heavily contaminated with a range of heavy metals derived from historical smelting activity (most notably Pb), to examine the applicability of FIRS at field-scale for site remediation and groundwater containment, and develop initial models of best-practice for its implementation at contaminated sites.

CONCLUSION

The FIRS technology, while still at prototype, bench-top scale, shows considerable promise as a technique for soil engineering, groundwater protection and contaminated site remediation.

The technique generates a resealable iron-rich barrier, which can be remotely placed (without engineering) to physically inhibit (or redirect) subsurface pollutant migration, and adsorb contaminants from ground or soil water.

The FIRS technology is also capable of significantly reducing contaminant concentrations in treated soil.

In addition, the technique can improve the mechanical properties of soils (contaminated or otherwise) for civil engineering purposes, via iron cementation and/or strategic electro-osmotic dewatering or rewatering.

CONCLUSION

FIRS has significantly lower energy requirements than commercial electrokinetic remediation techniques, uses low cost sacrificial (scrap iron) electrodes, and does not involve the use of potentially toxic conditioning solutions.

The technique is applicable to small sites, as well as to larger areas of contaminated land, and can be implemented in ground where man-made structures are present, or where there is on-going site activity.

Practically, the system can be operated in combination with, or as an alternative to, existing land remediation technologies, although it is probably best applied as a low-energy, non-selective, preliminary contaminant reduction / containment technique before the application (if necessary) of more specialist (and expensive) techniques.

Based on bench-top studies, the technique seems particularly applicable to soils and sediments contaminated with Cu, As, Pb and Zn.

The next step therefore is to upscale the technique and test its applicability in field trials on a heavy-metal contaminated site, a process being undertaken in the recently-approved CL:AIRE project RP15.

ACKNOWLEDGEMENTS

The authors are grateful to CL:AIRE for advice on the potential applications of the FIRS technique. The technique and ideas described here are the subject of a patent application filed in September 2002 by the Universities of Sussex and Brighton. Part of this work was completed under funding provided by EPSRC (grant number GR/S27924/01).

Paper presented to the CL:AIRE Annual Project Conference, April 20th 2004

Ferric Iron Remediation and Stabilisation (FIRS) – developing a new electrokinetic remediation technique for heavy metal- and As-contaminated sites.

Andy Cundy[1] **and Laurence Hopkinson**[2]

[1] *Centre for Environmental Research, University of Sussex, UK*
[2] *Division of Civil Engineering, University of Brighton, UK*

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ABSTRACT

Electrokinetic remediation is an emerging technology that has generated considerable interest as a technique for the *in-situ* remediation of clay-rich soils and sediments. Despite promising experimental results, however, at present there is no standardised universal electrokinetic soil/sediment remediation approach. Many of the current technologies are technically complex and energy intensive, and geared towards the removal of 90% or more of specific contaminants, under very specific field or laboratory-based conditions. However, in the real environment a low-tech, low-energy contaminant reduction / containment technique may be more appropriate and realistic. Such a technique, FIRS (Ferric Iron Remediation and Stabilisation), is described here. The FIRS technique involves the application of a low magnitude (typically less than 0.2V/cm) direct electric potential between two or more sacrificial, iron-rich, electrodes emplaced either side of a contaminated soil or sediment. The electric potential is used to generate a strong pH (and Eh) gradient within the soil column (pH 2 – 13), and force the precipitation of an iron-rich barrier or "pan" in the soil between the electrodes. Geochemical and geotechnical data for FIRS-treated sediments from Southampton Water and the Ravenglass estuary, U.K., and from a former wood preservation site in Scandinavia, are presented here and indicate that the technique can significantly reduce heavy-metal contaminant concentration in treated soil, by remobilisation of contaminants followed by precipitation on, or around, an iron-rich barrier. In addition, arsenic seems highly amenable to the FIRS treatment, due to its solubility under the high pH conditions generated near to the cathode, and its marked geochemical affinity with the freshly precipitated iron oxides and oxyhydroxides in the iron barrier. Geotechnical tests indicate that the iron barrier produced by the technique is practically impervious (permeability = 10^{-9} m/s or less), and has moderate mechanical strength (UCS ~ 11 N/mm^2). Notably, a large increase in shear strength in the treated soil near to the anode electrode (due to iron cementation and/or electro-osmotic dewatering) is also observed, without significant loss of porosity. The data indicate that the FIRS technique shows considerable promise as an *in-situ* method for contaminated land remediation and soil water containment, and can also be used to improve the mechanical properties of soils (contaminated or otherwise) for civil engineering purposes. A recently approved CL:AIRE project will upscale the existing bench-top scale work carried out on FIRS, and examine the applicability of the technique in the *in-situ* remediation of small to medium-scale working sites - specifically suburban back-garden sites contaminated by lead and other heavy metals.

INTRODUCTION

Although clays and silts at contaminated sites tend to sequester large quantities of heavy metals, radionuclides, and selected organic pollutants, they are relatively resistant to remediation with traditional technologies (e.g. pump and treat, soil washing) because of their low hydraulic conductivities. This has stimulated a considerable amount of research into cost-effective, in-situ techniques that can be used to remediate low-permeability, high clay content soils. One emerging technology that has received much attention is electrokinetic remediation. Electrokinetics is a process that separates and extracts organic, inorganic, and radioactive contaminants from saturated or unsaturated clay-rich soils, sludges and sediments under the influence of an applied electrical field. In its most basic form, the electrokinetic process involves the application of a low intensity direct current across electrode pairs that have been implanted in the ground on each side of a contaminated soil mass. Groundwater is dissociated at the electrodes, which produces an acid front (due to excess H^+ ions) around the anode and an alkaline front (due to excess OH^- ions) at the cathode. The electric current causes electro-osmosis and ion migration, which moves both water and aqueous phase contaminants in the subsurface from one electrode to the other, and electrophoresis, which results in migration of colloidal fractions. Aqueous phase contaminants, and contaminants desorbed from soil particles, are transported towards the anode or cathode depending on their charge. In addition, since the electrokinetic process results in the forced migration of water (electroosmosis), the electrokinetic process may also be used for civil engineering applications, particularly the dewatering of large volume slurries and waterlogged soils (e.g. Lamont-Black 2001).

In existing commercial electrokinetic land remediation systems, contaminants are commonly extracted by a secondary recovery system or deposited at the electrode. Surfactants, complexing agents, and other reagents are frequently used to assist contaminant movement. Despite promising experimental results, however, at present there is no standardised universal electrokinetic soil/sediment remediation approach. Instead there are a number of technologies (e.g., Lasagna™, Electro-Klean™, electrochemical geooxidation), each of which has different strengths, drawbacks, and operational and design requirements (Virkutyte et al., 2002). Many of the current technologies are technically complex and energy intensive, and geared towards the removal of 90% or more of specific contaminants, under very specific field or laboratory-based conditions. However, in the real environment a low-tech, low-energy contaminant reduction / containment technique may be more appropriate and realistic. Such a technique is discussed here.

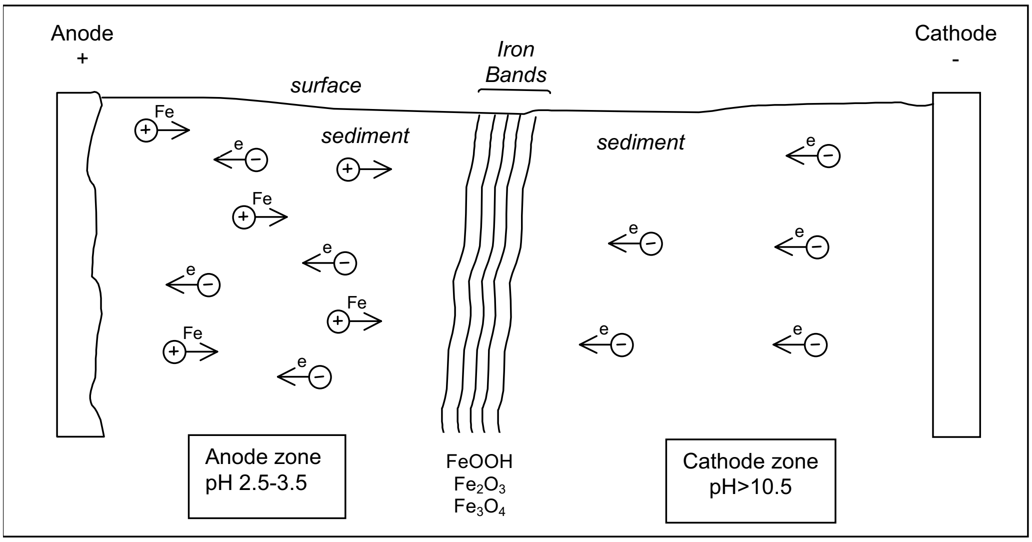

FIGURE 1: Generation of iron bands between sacrificial iron electrodes buried in a soil / sediment column. Adapted from Jacob *et al.* 1996.

THE FIRS TECHNIQUE

The FIRS technique (Ferric Iron Remediation and Stabilisation) involves the application of a low magnitude (typically less than 0.2V/cm) direct electric potential between two or more sacrificial, iron-rich, electrodes emplaced either side of a contaminated soil or sediment. The electric potential is used to generate a strong pH / Eh gradient within the soil column, and force the precipitation of an iron-rich barrier in the soil between the electrodes at the boundary between the acid and alkaline “fronts” (figure 1). The system mimics natural mineralisation processes, where internal electric fields present in rock and soil bodies can generate multiple bands of ironstone via precipitation of iron oxides and hydroxides (e.g. Jacob et al 1996). In the FIRS technique, these iron-rich bands are grown over timescales of 3 – 400 hours, and consist of amorphous (or microcrystalline) iron “pans”, or, in sandy soils, a coating of goethite, magnetite and zero-valent iron which cements mineral grains. Pilot studies on the FIRS technique have been applied at laboratory scales in 25×2×15cm and 30×50×40cm open topped perspex cells (i.e. effectively in two dimensional and three dimensional space). All experiments have been run at <5 volts, using sacrificial cast iron electrodes, in a variety of sands and contaminated muds, with groundwater and seawater interstitial pore waters, under unsaturated, and saturated conditions. Time scales ranged from 3-400 hours. In every case a 1-4cm thick, coherent, iron stone was generated *in situ*, approximately equidistant between cathode and anode. It is also possible to generate a dispersed sorptive coating of iron on a pre-defined area of soil, simply by switching off the current before the Fe-band fully develops.

Results from three of these bench-top studies illustrate the potential of the FIRS technique for contaminated leachate confinement and contaminated land remediation:

(a) Hydrocarbon and Cu contaminated sediments, Southampton Water

An estuarine mud sample from Southampton Water, contaminated with Cu and hydrocarbons from the nearby Fawley oil refinery and local shipping, was treated at 2V, in a 3D cell using a rectangular electrode array. A continuous iron band of up to 3cm thickness was generated from the electrode point sources. Data for pre- and post-treatment Cu concentration indicate that the electrokinetic treatment resulted in a ~61% or greater reduction in Cu contamination in the anode zone in 16.3 days (note that a small proportion of copper in these samples is natural background copper locked away in stable mineral interiors). In addition, liquid hydrocarbon-rich effluent was expelled from the sediment (via electroosmotic purging) and channelled and drained at *ca*. 10ml per day from the surface of the cathodic compartment. The energy requirement for the experiment was 10.9 kW/m^3. These values compare favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g., 500kW/m^3 for 100% removal of metal contaminants (Virkutyte et al., 2002). The time scale for copper decontamination of the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective membranes. The use of cast iron electrodes (as opposed gold coated, platinum or graphite electrodes), means that the experimental system is low cost in terms of energy, materials and electrode construction, which typically make up ~70% of the costs associated with any electrokinetic remediation system.

(b) Radioactively-contaminated sediment, Ravenglass, Cumbria.

A clay-rich sediment sample, slightly contaminated with radionuclides derived from the Sellafield nuclear facility, was collected from the Ravenglass estuary, Cumbria and treated at 1.5V for 410 hours in a 2D perspex cell (using an electrode separation of 17cm). A 17mm thick Fe-rich band was generated 5cm from the anode, at the point where a major step in pH (from pH 2 to pH 13) occurred. Geochemical and radiometric analysis of the treated sediment (figure 2) show clear removal of ^{60}Co from the anode zone of the cell, and precipitation of the remobilised ^{60}Co on, and in the cathode zone adjacent to, the iron-rich band (possibly co-precipitated with Mn, or precipitated as a hydroxide phase). Mn, Ca and Sr were also remobilised from the anode zone and precipitated on, or around, the iron band. Notably, As, present as a trace contaminant in these sediments, was highly amenable to the FIRS treatment, with desorption occurring at high pHs in the cathode zone. A 100% enrichment of As occurred on the iron-rich band (figure 2), reflecting the strong affinity of As for Fe. Geotechnical tests on the precipitated iron pan indicate a major loss of permeability following iron band formation - initial permeability of the untreated clay-rich sediment was ~ 0.3 x 10^{-7} m/s, whereas treated material permeability (in the precipitated iron band) was recorded at 10^{-9} m/s, or less, i.e. practically impervious. The approximate Uniaxial Compressive Strength of the iron band was 10.8N/mm^2 (comparable to, for example, a moderately lithified sandstone). Geotechnical test data also indicated a large increase in shear strength in the anode zone sediment following treatment, without any significant loss in porosity. SEM analysis of the treated anode zone sediments shows clear evidence for precipitation of iron oxides as a thin coating over mineral grains (figure 3). These data therefore indicate that a significant improvement in the engineering properties of the anode zone sediments has occurred, probably as a consequence of cementation via precipitation of iron (and/or through electro-osmotic dewatering). These data are discussed in detail elsewhere (Cundy and Hopkinson, submitted). While many of these tests, due to the small sample size available, were performed on non-ideal sample volumes, the results are supported by subsequent data for similar intertidal sediments run in larger volume, three dimensional cells.

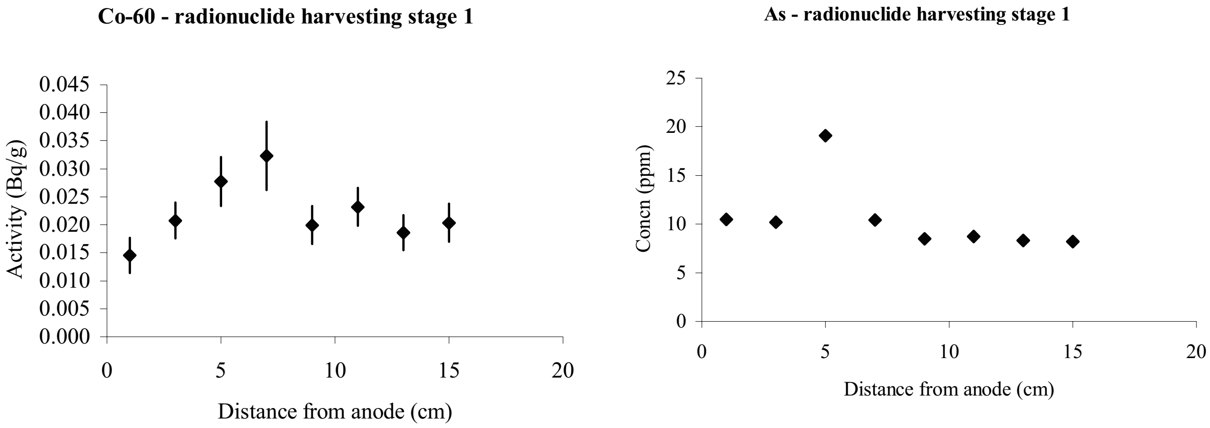

FIGURE 2: ^{60}Co and As data for treated Ravenglass mud. Fe band is located 5cm from the anode.

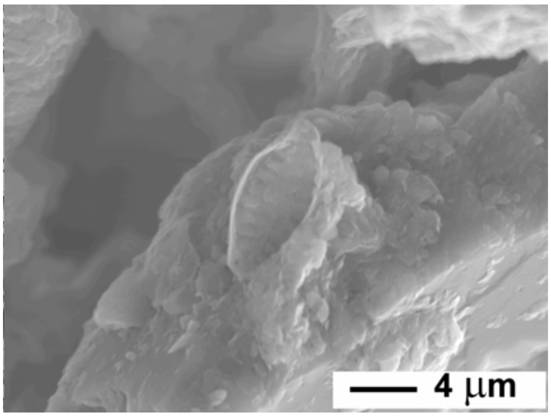

FIGURE 3: SEM image of Ravenglass sediment, showing diatom (marine microorganism) which, together with the underlying silt particle, has been coated and cemented by iron following treatment by the FIRS technique. Sample taken from the anode zone, at 3cm distance from the anode.

(c) Heavy metal contaminated waste spoil, Scandinavia.

A hematite (iron-oxide)-rich waste spoil, contaminated with As, Cu, Pb and Zn, was collected from a former wood preservation site in Scandinavia, and treated for 29 days at 2V in a 3D Perspex cell. A strong pH gradient developed relatively rapidly in the treated soil and became more pronounced over time, although a sharp pH jump of the type normally observed was not produced, presumably due to a buffering effect exerted by the soil. Hence, a discrete, clearly-visible iron band did not form over the timescale of the experiment, although the continuous drop in pH and expansion of the acidic anode zone over the course of the experiment indicate that with longer treatment periods the precipitation of a distinct Fe-band would be induced. Notwithstanding this, a highly alkaline zone and an acid zone were clearly generated in the cell, which caused significant remobilisation of As, Cu, Pb and Zn. Arsenic showed clear remobilisation from both the acidic anode zone and the alkaline cathode zone, with apparent precipitation of As phases at approx. 10cm distance from the cathode (at ca. pH 8 – 9) (figure 4). The net enrichment of As in this central band of the cell was 63% (compared to the cathode zone) and 30% (compared to the alkaline zone). Copper showed clear remobilisation from the acidic anode zone and apparent precipitation at approximately 16cm from the cathode (at ca. pH 6-7) (figure 4). Zinc and Pb also showed (a less pronounced) remobilisation from the anode zone. Neither zinc nor copper were remobilised from the cathode zone. Hence, despite the heterogeneity and mineralogical characteristics of the spoil (which effectively make the contaminated material a “worst case scenario” in the application of electrokinetic techniques), the FIRS treatment has successfully caused a reduction in the concentration of a range of contaminants (albeit without the formation of a distinctive iron band).

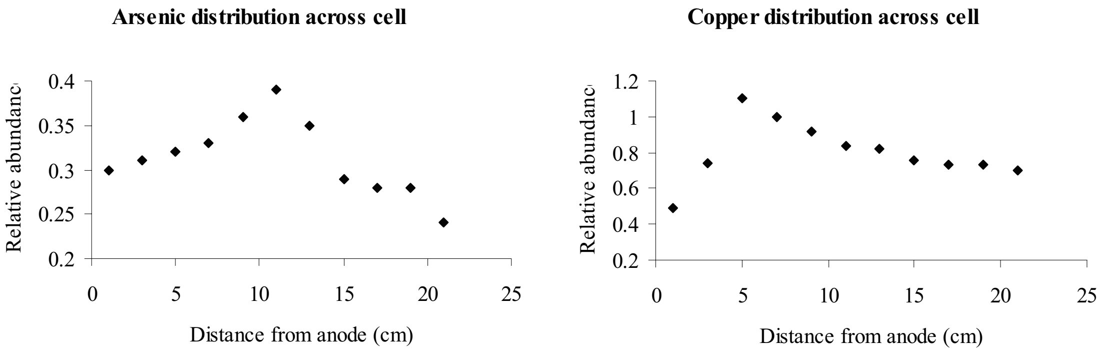

FIGURE 4: Arsenic and copper distribution across FIRS test cell, for hematite-rich waste spoil. Values given are relative rather than absolute.

TOWARDS A FIELD-BASED TECHNIQUE – CL:AIRE PROJECT RP15

The FIRS technique has significant potential for field-scale use, as it has already been successfully applied in decimetre-scale three-dimensional cells, and mimics a natural system that operates over scales in excess of 100 metres in geological systems. The low voltage and current used mean that power requirements are likely to remain low even when the system is upscaled, and, coupled with the flexibility provided by the use of multiple, low cost electrodes, means that contaminated land can be sequentially treated with a series of electrode arrays, placed to avoid (or work around) site infrastructure, where the distance between individual electrodes does not exceed a few metres. The recently approved CL:AIRE project RP15 will examine the use of the FIRS technique in remediating small working sites with relatively shallow contamination depth, as a first step in the development of the technique for field-scale use. The primary aim of this research project is to develop the FIRS technology from prototype stage (i.e. bench-top scale) and test it at field scale – specifically at two heavy-metal contaminated, suburban garden sites in south Yorkshire. The project consists of two phases: Phase 1 (field-scale laboratory trials), in which the existing FIRS system will be upscaled to treat metre-scale soil columns, and its remediation efficiency optimised for contaminated soil material from the proposed field-test sites; Phase 2 (field trials), in which the FIRS system will be tested at two suburban garden sites (in south Yorkshire) which are heavily contaminated with a range of heavy metals derived from historical smelting activity (most notably Pb), to examine the applicability of FIRS at field-scale for site remediation and groundwater containment, and develop initial models of best-practice for its implementation at contaminated sites.

CONCLUSION

The FIRS technology, while still at prototype, bench-top scale, shows considerable promise as a technique for soil engineering, groundwater protection and contaminated site remediation. The technique generates a resealable iron-rich barrier, which can be remotely placed (without engineering) to physically inhibit subsurface pollutant migration, and adsorb contaminants from ground or soil water. The FIRS technology is also capable of significantly reducing contaminant concentrations in treated soil. In addition, the technique can improve the mechanical properties of soils (contaminated or otherwise) for civil engineering purposes, via iron cementation and/or strategic electro-osmotic dewatering or rewatering. FIRS has significantly lower energy requirements than commercial electrokinetic remediation techniques, uses low cost sacrificial (scrap iron) electrodes, and does not involve the use of potentially toxic conditioning solutions. The technique is applicable to small sites, as well as to larger areas of contaminated land, and can be implemented in ground where man-made structures are present, or where there is on-going site activity. Practically, the system can be operated in combination with, or as an alternative to, existing land remediation technologies, although it is probably best applied as a low-energy, non-selective, preliminary contaminant reduction / containment technique before the application (if necessary) of more specialist (and expensive) techniques. Based on bench-top studies, the technique seems particularly applicable to soils and sediments contaminated with Cu, As, Pb and Zn. The next step therefore is to upscale the technique and test its applicability in field trials on a heavy-metal contaminated site, a process being undertaken in the recently-approved CL:AIRE project RP15.

ACKNOWLEDGEMENTS

The authors are grateful to CL:AIRE for advice on the potential applications of the FIRS technique. The technique and ideas described here are the subject of a patent application filed in September 2002 by the Universities of Sussex and Brighton. Part of this work was completed under funding provided by EPSRC (grant number GR/S27924/01).

REFERENCES

Cundy A.B. and Hopkinson L. Electrokinetic iron pan generation in unconsolidated sediments: implications for contaminated land remediation and soil engineering. Applied Geochemistry, submitted.

Jacob K-H, Dietrich S, and Krug H-J 1996. Self organised mineral fabrics. In: Kruhl J.H, Fractals and dynamic systems in geoscience. Springer Verlag, Berlin, 259-268.

Lamont-Black J. 2001. EKG: the next generation of geosynthetics. *Ground Engin*. October 2001, 22-23.

Virkutyte J, Sillanpaa M, and Latostenmaa P 2002. Electrokinetic soil remediation – a critical overview. *Sci. Tot. Env*. 289, 97-121.

Biographical Note

Colin Hills

Dr Colin Hills is a Reader in the University of Greenwich and Director of the Centre for Contaminated Land Remediation. After graduating Dr Hills worked as a field geologist and then in the construction materials industry before gaining his PhD in environmental engineering at Imperial College. With more than 20 years research and development experience, his interests include the stabilisation/solidification (S/S) of hazardous waste and contaminated land, the use of geomaterials in environmental applications and the beneficial re-use of waste materials. Dr Hills is principal investigator of the CASSST (Codes and Standards for Stabilisation/Solidification Technology) initiative, which has produced the UK guidance on S/S to be published by the Environment Agency later this year. Dr Hills is current Chairman of the Cement and Concrete Group of the Institute of Materials, Minerals and Mining and Chairman of Cement and Concrete Science.

Paper presented to the CL:AIRE Annual Project Conference,April 20th 2004

Performance Assessment of Stabilised/Solidified Waste Forms (PASSiFy)

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ABSTRACT

Stabilisation/Solidification (S/S) has been used to manage the risks associated with hazardous waste and contaminated land for approximately five decades. However, no systematic, detailed studies have been carried out to date on the durability of S/S waste forms in their environment of service. Consequently, an international team has been established to evaluate the performance of S/S wastes with time. In partnership with the environment agencies of the countries concerned, waste forms of varying age are being sampled in the USA, France and the UK and tested against their original acceptance criteria and examined with selected transversal testing procedures. The data obtained will be placed in a database, which will then be used in the construction of a risk management framework for enhanced stakeholder confidence.

INTRODUCTION

Stabilisation/Solidification (S/S) technology involves the mixing of binding agents into contaminated media, such as contaminated soil or hazardous waste to create a stabilised and solidified product. During S/S pollutants are chemically stabilised and physically encapsulated in the waste form. The technology is widely used as a risk management technique outside the UK.

In Europe, S/S is often used to treat hazardous and radioactive waste, however until recently, its application to contaminated land has been relatively limited, in France, for example, S/S has been routinely used since 1995, following the implementation of 1992 regulation for hazardous waste management, which introduced defined limits on pollutant leaching. Currently, about 400,000 T waste/year are treated by S/S.

The recent introduction of the EU landfill directive [1] will result in significant change in the way contaminated land and hazardous wastes are managed. It is anticipated that the application of cement-based S/S systems in the UK will increase significantly and this is reflected by the preparation of guidance on S/S technology by the Codes and Standards for Stabilisation /Solidification Technology (CASSST) initiative which will be published by the Environment Agency [2] in 2004.

Despite the widespread use of S/S outside the UK, particularly in North America [3], and even though the treatment has been in use since the 1950s [4,5], there are few data pertaining to the field performance of S/S waste forms.

In particular, there have been no co-ordinated field studies to verify the long-term effectiveness of S/S to treat waste for hazardous constituents, despite frequent requests from decision-makers (outside the UK) for verification of the long-term effectiveness of cement-based S/S [6].

However, the most significant research reported regarding the long-term effectiveness of S/S made the following observations and conclusions [7]:

- The extent of degradation after 6 years is considered slight to moderate, but at these rates the waste form may disintegrate over 50 to 100 years.

- Solidified/stabilised wastes are vulnerable to the same environmental degradation factors as concrete.
- Because the life of concrete products is finite and depends on the local environmental conditions, regulation for on-site burial of S/S treated wastes is needed.

The important omission of data from the literature is acknowledged by the US Environment Protection Agency (US EPA), who considers cement-based S/S as a best demonstrable available technology (BDAT) and proven for use with a wide variety of organic and inorganic contaminants. In the UK, reliable data on durability performance is seen as critical if S/S is to fulfill its potential as a reliable waste management technique for the remediation of contaminated land.

In recognizing the need for data on the durability of S/S wastes, the US EPA, the Environment Agency (England and Wales) (EA) and the Environment agency of France (ADEME) have agreed to join an international collaborative research program, together with a number of key commercial and academic research partners, namely the Centre for Contaminated Land Remediation, University of Greenwich, University of New Hampshire and INERTEC, supported by a number of organisations including SITA, Environmental Geotechnics, Land and Water, CL:AIRE, CIRIA, Portland Cement Association and Enviros Consulting. The aim of this collaboration is to improve our understanding of the long-term performance of cement-based S/S waste forms by retrieving and examining S/S materials of different ages from their environments of service.

OBJECTIVES

In the proposed work, a number of well-characterised waste forms of known age and location have been selected for study. These materials are supported by detailed information, including the nature of the contaminants treated, binding agents used and the results of treatabilty studies and contaminant characterisation testing.

The aim of this project is improved understanding and confidence in the long-term performance and effectiveness of S/S based on:

- An examination of samples taken from full-scale application of S/S technology
- Critical performance indicators identified from a detailed program of chemical, physical and microstructural testing
- The construction of a risk management toolbox for improved stake-holder confidence in S/S

PROGRAMME OF WORK

By testing waste forms against the original compliance criteria in their country of origin and a range of carefully selected testing regimes (transversal testing), a data-set will be constructed which will then be used in the development of models to predict the future behaviour of waste forms. This data set, supported by an examination of ancient cement-based materials as analogues, will be used to develop a risk management methodology or toolbox for improved stakeholder confidence. The data set will contain a range of spatial (microstructural, process) and temporal (cement set, long term performance assessment) data on different scales. As risk tools will be set within a risk management and decision framework, the output of PASSiFy will provide decision-makers with the tools necessary to assess the long-term effectiveness of S/S as a waste management strategy and allow the technology to be more widely used with confidence.

The investigation will be broken down into a number of information-gathering exercises and laboratory studies that form a series of coordinated tasks. The project co-coordinators in each region will gather data and enter the results onto a common database, which will provide a central comprehensive source of information for use during this project. The main tasks that will be carried out are given in Table 1.

Table 1 Tasks to be carried out by PASSiFy

Task	Description
1	Clarification of the history of use of each site
2	Determining site characteristics and identifying pollutant pathways
3	Sampling and performance testing to the original compliance criteria
4	Transversal testing using specialised techniques in each partner country
5	Interpretation of results and modeling studies
6	Reporting and dissemination of results
7	Risk management toolbox for improved stakeholder confidence

THE PROPOSED SITES

Ten former S/S sites will be evaluated in the USA, the UK and France. The majority of the materials treated and/or disposed in these sites contained mixed (organic and inorganic) contaminants and were primarily treated with cement or blended cement-binder systems.

In the USA, the US EPA has agreed to provide 5 sites of varying age for examination, the majority of which are SUPERFUND sites. These sites are well-characterised, Federal clean-up operations with considerable supporting documentation [e.g. 8-10]. Southern Company Services, Inc. is providing a sixth US site which is also well documented and monitored. Three other sites in the USA are being investigated for potential for inclusion in this work.

Five, suitable sites are available in Europe. In the UK, 3 sites have been identified with archived detailed supporting data; these are the ICI-owned Ardeer site in Ayrshire, Scotland (remediated by Bachy Soletanche), the Astra Pyrotechnics site in S.E. England (owned by University of Greenwich and remediated by Forkers), and the Union Canal near Falkirk, owned by British Waterways and remediated by Land and Water.

In France, hazardous waste treated by INERTEC is available near Paris and Angers (ex. SITA FD). These two hazardous waste landfill sites contain materials, which have been treated using blended binder systems.

The sites, for investigation in this program of study, vary from 17 years to 3 years in age. They are located in different geological and climatic regions and represent a number of distinct disposal scenarios, which are anticipated to provide invaluable data for the assessment of durability performance. Thus, generic processes for a range of environments, contaminants and treatments will be examined and used to establish the risk-based toolbox for predicting long-term S/S performance and improving stakeholder confidence.

Table 2 below lists the sites from which S/S waste will be removed and examined in this investigation.

Table 2. Sites to be investigated

Site	Date	Contaminants	Mix Design and Application
American Creosote Jackson, TN	1999	Creosote, PAH, PCP, Dioxins	5% Cement , 4.5% Fly Ash, 1.3% Carbon Ex-situ S/S
Manufactured Gas Plant, Columbus, GA	1992	PAHs, Cyanide, VOCs	10% Cement In-Situ S/S
Sapp Battery Alford, FL	1999 2000	Lead	6% Cement, 1% Phosphoric Acid Ex-Situ S/S
Schuykill Metals Battery Recycling Plant City, FL	1995 1996	Lead	10% est. Cement, 2% est. TSP Granules Ex-Situ S/S
Peak Oil Waste Oil Recycling Brandon, Tampa FL	2000 2001	Lead, Organics	5% Cement , 3% TSP Granules Ex-Situ S/S

Table 2. Continued

South 8th Street Waste Oil Recycling Sludge Pit. West Memphis, AK	1999 2000	Lead, Organics Acid	Neutralised with 25% $CaCO_3$ Treated with 20% Cement, 10% Fly Ash In-situ S/S
Selma Pressure Treating, Selma, CA	1993	PCP, Dioxins, CCA	Cement, Carbon, Bentonite, Proprietary Product Ex-Situ S/S
Network Underground Quarry Atlanta, GA (Georgia Power)	1995	PCB, metals, petroleum products	Cement, Bentonite, Slurry In-Situ S/S
Pepper Steel Hialeah, FL	1987 1988	PCB, Lead Arsenic	Cement, Fly Ash, Organophilic clay (15% in total) In-Situ S/S
Astra,Pyrotechnics, Dartford Kent	2000	Zinc, Lead, Nickel, Chromium	20% Cement Ex-Situ
Ardeer, Ayshire	1995	Silicon, Copper, Zinc	Cement, PFA In-Situ
Union Canal, Scotland	2000	Metals and organics	PFA and Cement Ex-situ,
Hazardous Waste Landfill, Paris	1994	Mixed metals	Proprietary Product Ex-situ
Hazardous Waste Landfill, Angers	2000	Mixed metals	Proprietary Product Ex-Situ

CURRENT STATUS

Substantial funding for the basic programme of work has been received in the UK and the USA to date. Three SUPERFUND sites have been sampled by the US EPA/University of New Hampshire with the remainder due for completion by the Autumn of 2004. Sampling, in the UK, will commence during the summer of 2004. A fourth UK site of 20 years in age, is currently being evaluated for inclusion in the project. PASSiFy has recently obtained CL:AIRE Approved Project Status.

DELIVERABLES

The work outlined in this research is designed to provide valuable data on the long-term performance of S/S technology so that the risks associated with applications of S/S technology can be quantified and effectively managed.

The main deliverables of the work are anticipated to be:

- Data to show whether S/S waste forms continue to meet their compliance criteria with time; Identification of risk or critical performance indicators from the assessment of waste form microstructure and phase chemistry;
- Knowledge and understanding of how the S/S waste forms are expected to behave in their environment of service over extended time-frames
- A commercially available risk management toolbox for improved stakeholder confidence in S/S technology.

Acknowledgements

This project has been put together with the assistance of Marie-Claire Magnie from INERTEC, Kevin Gardiner from the University of New Hampshire, Ed. Bates from the US EPA, Brian Bone from the Environment Agency and Laurent Chateau from ADEME. Key organizations also involved in PASSiFy include the University of Birmingham (Chris Rogers and David Boardman), the University of Cranfield (Simon Pollard).

REFERENCES

1) EU Council Directive 1999/31/EC of 26th April 1999 on the Landfill of Waste Official Journal L182, 16th July 1999 p 1-19.
2) www.cassst.co.uk
3) USEPA. 1986. Handbook of Stabilisation/Solidification of Hazardous Wastes. EPA/540/2-86/001.
4) Klich, I., Wilding, L.P. and Drees, L.R. 2002. Trace Metal and Mineral Speciation of Remediated Wastes Using Electron Microscopy. *Analytical and Bioanalytical Chemistry*, 372, 3, pp. 436-443.
5) Conner, J.R., Hoeffner, S.L. 1998. A Critical Review of Stabilization/Solidification Technology. *Critical Reviews in Environmental Science and Technology*, 28, 4, pp. 397-462.
6) Kirk, D.R. 1996. Summary of U.S. EPA Research on Solidified/Stabilized Waste from Long-Term Durability. ASTM STP 1240 (Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes), pp. 239-250.
7) Klich, I., Batchelor, B., Wilding, L.P. and Drees, L.R. 1999. Mineralogical Alterations that Affect the Durability and Metals Containment of Aged Solidified and Stabilized Wastes. *Cement and Concrete Research*, 29, 9, pp. 1433-1440.
8) Bates, E.R. and Lau, M.C. 1995. Full-scale Stabilization of Soils Contaminated with CCA and PCP at the Selma Pressure Treating Site, Selma, CA. Proc. Air and Waste Management Association, June 18-23.
9) USEPA. 1989. “Technology Evaluation Report SITE Program Demonstration Test, HAZCON Solidification, Douglassville. EPA /540/A5-89-001 (1989)10) U.S. EPA “HAZCON Solidification Process, Douglassville, PA: Applications Analysis Report,” EPA /540/A5-89-001