

Contaminant Source Zone Characterisation and Remediation

A meeting convened by The Hydrogeology Group of The Geological Society
University of Sheffield, Wednesday 22nd April 2009
Final Programme and Joining Instructions

Final programme and abstracts

The final programme of oral and poster presentations for this meeting is provided overleaf, with abstracts.

Joining instructions

Meeting venue

The venue for this meeting is Mappin Hall, in the Department of Civil & Structural Engineering within the Sir Frederick Mappin Building, located on Mappin Street on the University of Sheffield campus. The venue is marked as building no 170 (**see red star**) in the yellow sector on the attached map of the university campus. This and other maps of Sheffield can also be accessed at

<http://www.shef.ac.uk/visitors/mapsandtravel>

When you enter the Sir Frederick Mappin Building from Mappin Street (adjacent to church), proceed straight ahead up one flight of stairs. Mappin Hall should then be immediately in front of you on the first floor. Signs will be posted to guide you and there are porters (porters lodge on left) at the entrance to the building who can assist. On arrival at Mappin Hall, please register at the desk, pay the appropriate registration fee (you will need your Geological Society membership number or student ID card, if applicable for this) and collect your name badge. Cheques should be made payable to the **Hydrogeological Group of the Geological Society**. Receipts will be provided for all payments.

Travel to Sheffield

There are good rail and road links to Sheffield. If travelling by train, the simplest way is to connect by tram (outside Sheffield rail station) to the Broad Lane roundabout (refer to map), followed by a short walk (10 minutes) down Broad Lane to the meeting venue. Alternatives are a taxi or walk from the rail station (allow 15-20 minutes).

If travelling by car, exit the M1 at jct 33 (south and central Sheffield) and follow signs for the city centre, then on to University of Sheffield campus (allow 20 minutes for this). The map (see website above) also shows public car parking areas (pay and display) plus directions if you are not familiar with the city.

Accommodation

If you require overnight accommodation, there are a variety of hotels within 10-15 minutes walk of the meeting venue. The following websites may be useful:

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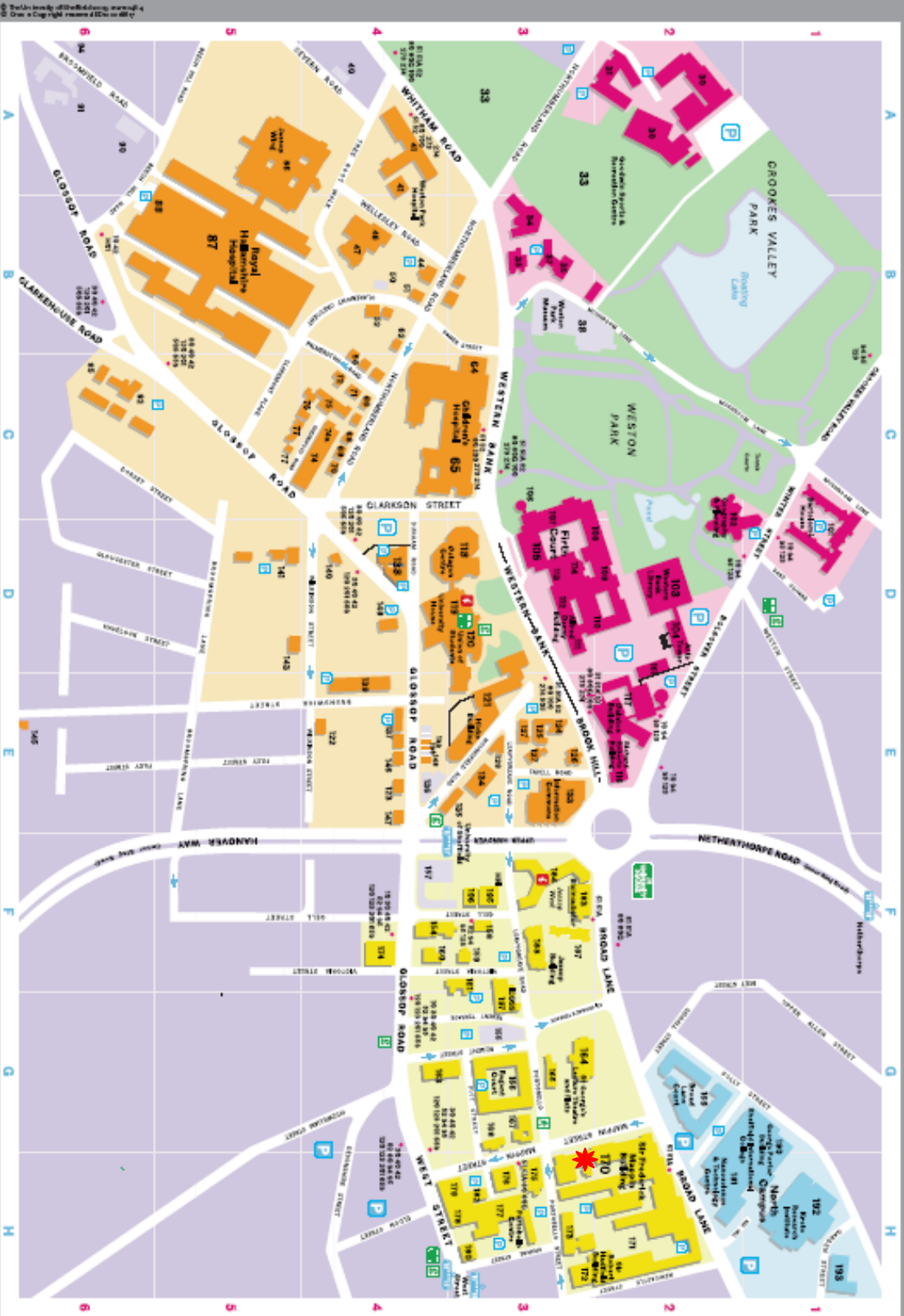
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If you have any questions, please contact the conveners

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S10 2TL. This takes you to the main Western Bank part of the campus, map reference D5.

Programme of oral and poster presentations	
Time	
09.30	Registration and coffee
	Morning session – chaired by Steve Thornton
10.15	Introduction by Steve Thornton
10.20	<i>DNAPL source zone remediation: How certain are we of success?</i> GP Wealthall, M Cave, R White, JE Chambers, M Lelliott, MO Rivett & P Zeeb (British Geological Survey & University of Birmingham, UK)
10.50	<i>Triad approach to redefine a site conceptual model: MIP investigation of a DNAPL source area</i> JP Davit, D Chiarbonello, F Pioveno & P Kociolek (Golder Associates, Italy)
11.15	<i>Secondary Source Zones: Towards an understanding of contaminant rebound</i> R White, GP Wealthall, M Lelliott, D Noy & RD Wilson (British Geological Survey & University of Sheffield, UK)
11.40	<i>Bromate contamination in the Hertfordshire Chalk: characterising and quantifying the source term and its impacts on predictions of long-term contaminant concentrations.</i> CM Fitzpatrick, SJ Cook, JA Barker & WG Burgess (University College London & University of Southampton, UK)
12.05	<i>Use of the modified Waterloo Profiler™ to provide high-resolution vertical and lateral delineation of groundwater impact from volatile organic compounds (VOCs)</i> J Baldock, P Crowcroft, A Peacock, A Sykes & A Thomas (ERM, UK)
12.30-13.45	Lunch and poster session
	Afternoon session – chaired by Steve Buss
13.45	<i>Improved approaches for performance assessment monitoring of contaminant source zones</i> RD Wilson & Z Cai (University of Sheffield, UK)
14.15	<i>Geophysical characterisation and monitoring of a TCE source zone during bioremediation</i> JE Chambers, PB Wilkinson, RD Ogilvy, R White & GP Weathall (British Geological Survey, UK)
14.40	<i>Field Demonstrations of in situ smouldering as a remediation technology</i> C Switzer, P Pironi, G Rein, JL Torero & JI Gerhard (University of Edinburgh & University of Strathclyde, UK, University of Western Ontario, Canada)
15.05-15.35	Break and poster session
15.35	<i>Characterisation of dioxin speciation to separate contaminant sources and modes in order to facilitate site remediation</i> R Lansley (Golder Associates, UK)
16.00	<i>Beneficial hydraulic fracture propagation during in situ chemical oxidation</i> SA Mathias, AP Butler, G Fowler, I Fielding, A Shields, J Barber and P Daly (Imperial College, London, Worley Parsons, Environment Agency & National Grid Property Holdings Ltd, UK)
16.25	Meeting close

Poster presentations

An optimisation approach for groundwater monitoring network augmentation - a 'detection' monitoring case study

K Azimi (Coffey Geotechnics, UK)

Trichloroethene: A potential groundwater tracer to characterise hydrophobic contaminant transport

G Barns, SF Thornton, RD Wilson & N Thomson (University of Sheffield & University of Waterloo, Canada)

Mixed technology remediation of a former chemical works, Manchester, UK

AJ Dunhill & S Edgar (Wardell Armstrong & S VertaseFli Ltd, UK)

Groundwater risk assessment without source term data

J Dottridge & L Heaney (Mott MacDonald, UK)

Groundwater modelling of plume rebound around TCE NAPL zone in support of source removal

H Fraser & W Wood (ESI Ltd, UK)

Source zone characterisation and the influence of aquitard topography on DNAPL distribution

H Fraser & H Streetly (ESI Ltd, UK)

Assessment and enhancement of hydrocarbon natural attenuation using biofilms

K Hampson, S Kelly & B Reid (University of East Anglia, UK)

Investigating LNAPL drop hysteresis: Implications for residualisation and source zone assessment

J Heneghan & RD Wilson (University of Sheffield)

The effectiveness of chemical oxidation to remediate DNAPL in fractured porous media evaluated via numerical simulations

T Pang, J Gerhard & B Kueper (University of Edinburgh & Queens University, Canada)

Case study of iterative modelling to predict the location and size of an off site chlorinated solvent source zone

M Plimmer (Geotechnical & Environmental Associates, UK)

DNAPL source zone remediation: How certain are we of success ?

G.P. Wealthall, M. Cave, R. White, J. Chambers, M. Lelliott (British Geological Survey, Nottingham, UK), M. Rivett (University of Birmingham, UK) and P. Zeeb (Geosyntec Consultants, Acton, MA, USA)

Contamination of groundwater by chlorinated solvents over the last century charts an historical legacy of dense non-aqueous phase liquid (DNAPL) production, distribution and end-use. Scientific endeavour over the past few decades, involving empirical studies, numerical modelling and remediation trials, has advanced understanding and contributed to our abilities to remove significant contaminant mass from the subsurface. However, concerns regarding partial DNAPL mass removal, which may leave groundwater contaminated above acceptable limits, remains a major uncertainty in determining the feasibility of DNAPL source zone remediation.

Measuring and predicting the success of the clean-up of DNAPL contaminated sites is receiving increasing focus from site owners, practitioners and regulators. A logical starting point for this measurement is the estimation of total mass existing prior to (and after) remediation. However, the detection and delineation of the DNAPL source zones is not trivial and small-scale sub-surface spatial variability (heterogeneity) can introduce substantial uncertainty in the estimation of DNAPL mass. At most sites the spatial architecture of the DNAPL is invariably poorly known due to technical and financial investigation constraints.

Here we describe the primary characteristics of DNAPL source zones, outline the tools that are available to map DNAPL source zone architecture and quantify contaminant mass depletion, and examine the relative merits of a number of remediation performance metrics. A case study from the Source Area BioREmediation (SABRE) site, an industrial site in the UK Midlands with as historic TCE DNAPL source, is presented that illustrates the application of the USEPA Type II Metric – the difference between the estimated initial and final mass. Mass estimates are presented for contrasting site investigation densities, including a sparse borehole network at the site scale and dense borehole network installed in the SABRE research cell. Sensitivity analysis of the input parameters to the mass estimate algorithm demonstrates the importance of expressing uncertainty in quantifying the initial and final mass estimates.

Triad approach to redefine a site conceptual model: MIP investigation on a DNAPL source area

J.P. Davit, D. Chiarbonello, F. Piovano and P. Kociolek (Golder Associates Srl, Torino, Italy)

A sound and detailed Site Conceptual Model (SCM) is the key for every successful remediation project. Golder Associates used the Triad approach to collect an integrated hydrogeological and chemical dataset on a DNAPL source area, already subject to remedial actions. The investigations leveraged all three elements of Triad: systematic planning process involving stakeholders, real-time in situ measurements (using Membrane Interface Probe or MIP investigation coupled with traditional soil sampling) and a dynamic work strategy, allowing to modify the work plan during the field activities. The Site is a manufacturing facility located in the eastern Po plain, and is underlain by a succession of sand and silt layers. Chlorinated solvents such as 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), perchloroethylene (PCE) have been used in the past. Chlorinated solvents were detected in groundwater over an extensive portion of the Site at concentrations higher than 50 mg/l and several source areas were suspected. A semi-quantitative evaluation of the extent of the impacted areas was done by means of over 7,000 MIP readings, which were verified against grain-size as well as soil and groundwater analytical results. MIP investigations were crucial in identifying the contaminant distribution, in the capillary fringe and in the saturated soil, as well as the effect that the different matrices have on contaminant migration. Furthermore, given the immediate analytical response, the investigation plan was modified and refined during the works without impacting the planned budget. 3D interpolation of the discrete MIP readings was used for managing the data and provided a consistent basis for the redefinition of a robust SCM and address the remedial options on a more realistic basis.

Secondary source zones: Towards an understanding of contaminant rebound

R. White, G.P. Wealthall, M. Lelliott, D. Noy (British Geological Survey, Nottingham, UK) and R.D. Wilson (University of Sheffield, UK)

Low permeability strata form capillary barriers that limit the downward migration of dense non-aqueous phase liquids (DNAPLs). The Mercia Mudstone Group comprises silty clays, which contain gypsum, siltstone and very fine sandstone. The deposits are typically weathered near surface, which is often associated with overlying minor aquifers including river terrace sands and gravels. Where DNAPLs, such as chlorinated solvents, are present in these hydrogeological settings, the contaminant is distributed between the immiscible phase and high concentration dissolved-phase mass. The clean-up of these fluvial aquifers depletes the primary source of contaminants, however, the underlying mudstone may provide a significant secondary source of contaminant

mass. The transfer of mass from the mudstone to the aquifer may extend remediation times and increase remediation costs. Results from the Source Area BioREmediation (SABRE) site indicate trichloroethene (TCE) occurrence within the weathered, fractured mudstone. Core samples recovered from the site record both diffusion dominated profiles and profiles indicating TCE DNAPL occurrence at depths approaching two metres below the mudstone surface.

This study reports an investigation of the mudstone characteristics that influence TCE mass removal flux between the mudstone surface and the overlying aquifer. 2-D numerical simulations, parameterised by field and laboratory data, examined the interplay of fracture spacing and fracture aperture on mass removal flux. Three modelling scenarios i) diffusion profile, ii) diffusion profile with high concentration linear fractured band and iii) constant high concentration profiles are indicative of conditions observed at the SABRE. Each scenario was examined to determine the effects of geological heterogeneity on contaminant mass removal. Simulations indicated that the mass flux entering the overlying aquifer would be degraded by enhanced bioremediation, however, the rate of flux at this boundary was highly dependent on the fracture spacing and aperture.

Bromate contamination in the Hertfordshire Chalk: characterising and quantifying the source term and its impacts on predictions of long-term contaminant concentrations

C.M. Fitzpatrick, S.J. Cook (University College London, UK), J.A. Barker (University of Southampton, UK) and W.G. Burgess (University College London, UK)

The Hertfordshire Chalk aquifer is affected by bromate contamination over an area of 40 km², the largest occurrence of point-source groundwater contamination in the UK. The source of contamination has been identified as a former industrial site. Investigation and monitoring data at the source is available for just 5 years of the potential 50 year history of the source.

Considerable effort has been directed at developing models of long-term, large-scale transport of bromate in Hertfordshire. However, there has been little consideration of the impacts uncertainty in the source term has on the reliability and applicability of these models. In order to address this, the available site investigation and monitoring data for the source site, and locations down-gradient of the source site, have been collated and reviewed. Various interpolation techniques have been used to estimate ranges of contaminant mass and concentration distributions at the site. These ranges are considered alongside a number of conceptual scenarios for bromate mobilisation and release to groundwater, and the potential for these mechanisms to produce the concentrations seen both at the source and down-gradient are being evaluated.

The bromate contamination in Hertfordshire is a pertinent example of the frequent requirement to make predictions of long-term pollutant concentrations with very little knowledge of the source term. In principle, given enough good-quality historical data on the downstream concentrations it is possible to 'back out' the source term. Modelling of synthetic data is being used to provide a basis for interpreting fracture and pore-water concentrations in the Chalk in order to determine the source input history.

Use of the modified Waterloo Profiler™ to provide high-resolution vertical and lateral delineation of groundwater impact from volatile organic compounds (VOCs)

J. Baldock, P. Crowcroft, A. Peacock, A. Sykes and A. Thomas (Environmental Resources Management, UK)

Following a programme of traditional site investigation and remediation works, undertaken by others at a former dye manufacturing facility, on-going surface water monitoring showed that concentrations of VOCs (principally trichlorobenzene and its degradation compounds) remained above statutory guidelines in a river located immediately adjacent to the site.

To develop a revised remediation strategy in order to facilitate site closure, ERM recommended refinement of the Conceptual Site Model (CSM) via additional intrusive investigation works to evaluate the significance of potential pollutant linkages between the site and the river. These works included an innovative groundwater contaminant investigation within the underlying heterogeneous drift aquifer, using a Modified Waterloo Profiler™ (MWP), for only the second time in the UK. The MWP is a direct push groundwater sampling device, advanced via Geoprobe™, which allows collection of the following discrete interval data:

- Geochemical parameters (pH, electrical conductivity, temperature, dissolved oxygen and/or oxidation-reduction potential);
- Hydraulic head;
- Relative changes in subsurface hydraulic conductivity; and

- VOC samples for rapid on-site laboratory analysis.

The use of the MWP enabled the investigation to be completed using a dynamic Triad style approach and provided real time geological, hydrogeological and chemical analysis data that were used to assist with determination of vertical sampling intervals and location of subsequent advanced MWP sampling points. This approach allowed the VOC plume to be defined more rapidly and at a lower cost than traditional techniques would have allowed.

The high-resolution of the MWP data significantly improved the accuracy of the previously developed CSM and allowed more accurate quantification of contaminant mass distribution and magnitude at the site, hence improving the likelihood of success and cost certainty of the additionally proposed remediation works. For example one MWP location drilled within 0.5m of a traditional monitoring well identified the presence of dense non aqueous phase liquid (DNAPL), whereas previously undertaken groundwater sampling of the well had identified relatively low dissolved phase concentrations and an absence of DNAPL.

Improved approaches for performance assessment monitoring of contaminant source and plume remediation

R.D. Wilson and Z. Cai (University of Sheffield, UK)

It is generally appreciated that NAPL source zone, especially those involving dense phases, exhibit complex spatial architecture, and yet monitoring strategies often disregard this. Regardless of the method used to remediate such sources, this complexity should be taken into consideration not just during the design and implementation phase, but also when evaluating treatment performance. Especially where engineered treatment is performed near source, the complex architecture generates spatially discrete dissolve phase signals. Conventional monitoring approaches, where long-screened wells are deployed with concentration-based performance metrics in mind, do show general trends but can obscure key process-level indicators of treatment.

A strategic approach was employed to monitor the treatment performance of two NAPL source areas, where the primary performance metric was based on quantifying mass flux. One site involved the aerobic biostimulation of a petrol LNAPL, and the other involved the anaerobic bioaugmentation and biostimulation of a chlorinated solvent DNAPL. At each site, multilevel groundwater sampling devices were installed in transects across a portion of the plume, as well as a number of conventional monitoring wells. The groundwater velocity field flowing across these transects was estimated from local gradient information and point specific estimates of hydraulic conductivity using falling head tests at the DNAPL sites and grain size analyses at the LNAPL site. The measured concentration of contaminant species was combined with velocity to generate estimates of total mass flux across the multilevel transects. The MLS point flux estimates were also kriged to create flux maps that revealed the locations where most bioactivity occurred. The temporal trends generated from the monitoring well data did not accurately represent changes in mass flux, and did not allow for a reliable assessment of key processes. Understanding of both rate of contaminant degradation and the location where that occurs allowed for adjustments to be made to the remediation system, particularly at the LNAPL site. Such performance monitoring approaches require a change in philosophy, and while increased cost will be incurred, the reliability of treatment efficiency assessments may well be worth it.

Geophysical characterisation and monitoring of a TCE source zone during bioremediation

J.E. Chambers, P.B. Wilkinson, R.D. Ogilvy, R. White and G.P. Weathall (British Geological Survey, Nottingham, UK)

Successful characterisation of DNAPL source zones is essential for determining DNAPL mass, designing effective remediation strategies, and for assessing the efficacy of treatment. Where significant subsurface heterogeneity exists, conventional intrusive investigations can be limited as the information they provide is restricted to vertical profiles at discrete locations, with no information between sample points. Therefore significant uncertainty can remain, both in terms of the lithological variability and the distribution of DNAPL. In order to mitigate this problem complimentary geophysical ground investigation methods such as electrical resistivity tomography (ERT) are being increasingly applied to these types of problems, as they have the advantage of producing spatial or volumetric information on subsurface variability.

In this study cross-hole ERT was used to characterise ground conditions and monitor changes within the SABRE test cell during a bioremediation experiment. The SABRE site comprises river terrace sand and gravel deposits overlying low permeability weathered mudstone bedrock. The surface of the site is overlain by alluvium, and a substantial thickness of made ground resulting from many decades of industrial use. ERT was

used to determine geological structure, and monitor changes in pore water EC during the remediation of TCE contamination. ERT transects were installed in both the source and plume zone, each comprising a fence of seven closely spaced borehole electrode arrays. Calibration of the ERT data was achieved by using borehole logs and geochemical data generated from multilevel sampler arrays that were located within the ERT transects. Baseline ERT scans were used to determine the geometry of the sand and gravel/bedrock interface, and were used to identify zones of high DNAPL saturation. Time-lapse ERT imaging was used to identify preferential flow pathways within the test cell, and changes in pore fluid EC related mainly to the delivery of amendments to aid remediation and, partially due to geochemical changes resulting from the dechlorination of DNAPL.

Field demonstrations of in-situ smouldering as a remediation technology

C. Switzer (University of Strathclyde, UK), P. Pironi, G. Rein, J.L. Torero (University of Edinburgh, UK) and J.I. Gerhard (University of Western Ontario, Canada)

Smouldering combustion is being developed as a remediation process for soils contaminated with non-aqueous phase liquids (NAPLs). Self-sustaining Treatment for Active Remediation (STAR) is particularly effective on high molecular weight NAPLs such as coal tars and heavy oils, which are among the most recalcitrant of industrial contaminants. Smouldering is a lower energy, flameless form of combustion that is oxygen-limited. Typical smouldering examples involve porous solid fuels that are destroyed by the smouldering reaction (e.g., a smouldering charcoal briquette or smouldering polyurethane foam in furniture that leads to a fire). The oxygen limitation occurs because the oxygen for the combustion reaction has to travel through the porous matrix (in the case of STAR, the soil) to reach the fuel (contaminant). STAR is proving to be particularly effective in the in situ destruction of contaminants, with little to no detectable residue remaining in many cases.

Upward scaling of the STAR process has not led to any loss in efficiency. Small-scale ex-situ field demonstrations were conducted on two different contaminant and porous media matrices to highlight the broad range of suitable conditions for STAR. The first trial used an idealised mixture of coal tar in coarse sand. Comparison of this field trial data to small and intermediate scale experiments suggests that process efficiency improves with scale. The relative airflow required by the process decreases as scale increases. The second field trial used an industrial mixture of oil wastes from a variety of sources, offering important insights into the effects of moisture and the mechanisms of heat transfer that influence the STAR process. This paper presents laboratory, intermediate and field-scale experiments in the context of the scaling process. Discussion focuses on the key parameters required for successful STAR as well as emissions characterisation for combustion by-products.

Characterisation of dioxin speciation to separate contaminant sources and modes in order to facilitate site remediation

R. Lansley (Golder Associates, Nottingham, UK)

This is a study comparing the speciation fingerprint of dioxin congeners to identify the contaminant source and hence contamination mode to identify rules and methodology for invoking remediation. The site of interest comprises a former effluent treatment plant which had received effluents containing dioxin. Whilst sludge containing dioxin was relatively easily identified and managed, the effluent from the treatment plant had historically been irrigated over paddocks, and there was no aesthetic impairment of the soil quality of irrigated soils. The toxic equivalent concentration of dioxin was measured in samples of soil obtained from these paddocks with the soil identified for remediation if it exceeded a benchmark concentration.

This project was concerned with the identification of contamination by dioxin in these paddock soils by depth and extent and the subsequent excavation and disposal of contaminated soil. Following measurement of dioxin in soils from both irrigated, un-irrigated and off site locations samples of soil from un-irrigated areas exceeded the toxic equivalent benchmark. On review of the congeners of dioxin present, those samples with elevated dioxin from depth or from un-irrigated areas identified a different congener species to those deriving from irrigated areas. The result of this was that the area of soil affected by irrigated effluent could be mapped in both depth and plan extent.

The irrigated source of dioxin was well known and hence the contamination mode was understood to be a point source that would require remediation on exceedance of the benchmark toxic equivalent. The second source of dioxin was less known and exceedance of the benchmark toxic equivalent concentration showed few trends by both plan and depth extent. Publications describing the regional background loading of dioxin in soil identified that in urban and industrial environments, diffuse pollution of dioxin deriving from fallout of atmospheric

particulates could provide a source of dioxin contamination. The speciation of this source was predominantly OCDD which is the same as the secondary source of elevated dioxin at the site.

The output of the project was the derivation of a statistical filter to separate the soils that were affected by point source, irrigation activities and diffuse sourced, regional atmospheric activities. Those samples identified to derive from the point source were mapped in plan and depth and excavated on a case by case basis. Those soil samples that were identified to derive from a diffuse source were considered as a statistical population to consider the likely exposure and compliance with the benchmark criteria

Beneficial hydraulic fracture propagation during in situ chemical oxidation

S.A. Mathias, A.P. Butler, G. Fowler (Imperial College London, London, UK), I. Fielding (WorleyParsons, Leeds, UK), A. Shields (WorleyParsons, Bristol, UK), J. Barber (Environment Agency, Leeds, UK) and P. Daly (National Grid Property Holdings Ltd, UK)

There is a continuous increase in the use of In-Situ Chemical Oxidation (ISCO) techniques for the treatment of contaminated sites in the UK. ISCO involves the direct delivery of chemical oxidants to contaminants residing in the subsurface such that rapid and total transformation to carbon dioxide or less toxic daughter compounds is achieved. Commonly used oxidants include permanganate (1.7V), hydrogen peroxide (1.8V), ozone (2.1V), persulfate (2.1V), activated persulfate (2.6V), and catalysed hydrogen peroxide (2.8V). Delivery is generally via an array of high pressure well-points. The spacing of injection points is generally planned on the basis that individual injection points produce a near-spherical plume of oxidant. As part of a Technology Strategy Board project, a set of intensely monitored ISCO injections of persulfate and catalysed hydrogen peroxide were performed at a contaminated site in the North of England. Observed variables included groundwater pressure, electrical conductivity, oxidant concentration, tracer concentration, redox potential, dissolved oxygen and pH. The observed spatial distributions of pressure and tracer indicated that the injected oxidant became distributed in areally extensive zones of limited vertical thickness. The site geology is relatively isotropic and homogeneous, hence such behaviour is postulated to be due to hydraulic fracturing. Hydraulic fractures are known to develop when pore pressures exceed the in situ minimum principal stress. ISCO injection typically occurs at relatively shallow depths (5 to 20 m below ground surface). Therefore hydraulic fracturing can be expected at relatively modest injection pressures. Interestingly, emplacing oxidant in thin self-driven hydraulic fractures is operationally preferable to spherical plumes due to the associated increase in surface area. In this paper, it is proposed that hydraulic fracturing is an improved delivery mechanism for ISCO and provides a new basis for injection-point array design.

An optimisation approach for groundwater monitoring network augmentation - a 'detection' monitoring case study

K. Azimi (Coffey Geotechnics, Manchester, UK)

Optimal design of site investigation and monitoring programmes realizes significant savings both in time and cost in most geoenvironmental projects. With the increasing cost of acquiring hydrogeological data, for example, optimisation and geostatistical approaches (as opposed to purely hydrogeological methods) are attracting more and more attention in designing 'detection' or 'compliance' monitoring networks. There is substantial evidence in the literature on successful application of Operations Research (OR) techniques in water resources and water quality management. A successful application of these methods in detection monitoring of hot spots of an oil contamination mound beneath an oil refinery in Iran will be demonstrated and discussed.

The Maximal Covering Location Problem is an integer-programming, heuristic method proposed in the literature primarily for optimal locating of a defined number of units provided for a public utility or service (e.g. ambulance dispatching centres) on a discretized network of demand nodes. The method is adopted to augment the pre-existing network of monitoring wells in the refinery (which had been installed for geotechnical purposes rather than detection monitoring) to detect the hot spots more cost-effectively. This augmentation in turn would direct the remediation resources more efficiently. The objective function is to maximise the areal coverage of the contamination mound by optimal locating of the added monitoring wells to prevent any gap and / or overlap in covering the mound by the monitoring wells. A geostatistical tool (stochastic interpolator) is used to estimate the nodal weights (concentrations) to inform the optimisation model. The result of the optimisation method is then implemented (i.e. the additional monitoring wells proposed by the model are installed). Finally, using the updated data from the augmented network of monitoring wells and by the use of the geostatistical tool, the contamination hot spots are detected.

Trichlorofluoroethene: A potential groundwater tracer to characterise hydrophobic contaminant transport

G.L. Barns, S.F. Thornton and R.D. Wilson (University of Sheffield, UK)

Dissolved organic pollutants originating from near ground source zones or NAPL plumes can be detrimental to human health, groundwater quality and the environment. The in-situ behaviour of contaminants cannot be easily predicted. Regulations often do not permit the addition of organic contaminants to an aquifer to characterise transport using tracer tests. Organic chemicals which are not considered toxic can be added to an aquifer during a tracer test to determine the fraction of organic carbon (*foc*), which is an important parameter in estimating the transport (e.g. retardation) and bioavailability of dissolved hydrophobic organic contaminants. Values of *foc* obtained can be used to estimate the aquifer natural attenuation capacity or design remediation schemes.

Trichlorofluoroethene (TCFE) is being evaluated as a potential new organic tracer for use in forced gradient tracer tests. TCFE is advantageous due to ease of measurement, low toxicity and appropriate hydrophobic properties. Laboratory batch tests, which include determination of the TCFE octanol-water partition coefficient and sorption behaviour in model systems containing sand and activated charcoal as the sorbent, have been performed. Preliminary results show that TCFE isotherms can be described by freundlich sorption behaviour over realistic organic solute concentrations and that sorption depends strongly on charcoal concentration. Column tests to up-scale this analysis and further assess the suitability of TCFE as a tracer under dynamic conditions will be outlined.

Mixed technology remediation of a former chemical works, Manchester, UK

A.J. Dunhill (Wardell Armstrong, UK) and S. Edgar (VertaseFli Ltd, UK)

The 6.5 Ha site was formerly used for refining crude tar and fractioning chemicals. The site has been in operation from the early 1900's and up until 1965. The process created a number of chemical intermediates (solvents, benzol, creosols, phenols, naphthalene, pitch and pyridines) and later tar. From 1965 the site changed uses and became a storage facility for heavy fuel oils and a chemical manufacturer.

The site investigations revealed free phase product in the surface water, solid lumps and shards of tar and a constant odour of phenol and naphthalene. Extensive contamination of 120,000 m³ of contaminated soil and 6000 m³ of groundwater with general aliphatic and aromatic hydrocarbons in the range C10 to C35 (up to 30,000mg/kg), benzene (0-100mg/kg), toluene(0-100mg/kg), xylene(0-2000mg/kg), phenols (up to 500mg/kg, and naphthalene(up to 1000mg/kg) and free phase product was identified.

Groundwater concentrations before remediation also included free product and general aliphatic and aromatic hydrocarbons in the range C10 to C35 (up to 1-50mg/l), benzene (100-20,000ug/l), toluene(0-1800ug/l), xylene(0-2000ug/l), phenols (up to 1000ug/l, and naphthalene(up to 3000ug/l).

A remedial strategy was developed to include site specific remediation criteria for both human health and the Environment to facilitate re-development of the site. This strategy called for significant remedial action to the site to depths up to 5m in soils and in groundwater over significant parts of the site. The contamination was significant and could not be mitigated with barriers and capping layer alone. The developer had a fixed timescale and budget.

A multi technology approach was used to manage all risks within a sustainable budget to allow the developer to progress to profitably re-developing of the site. Four main techniques were selected to manage risk appropriately:

- Ex-situ Bioremediation for Hydrocarbon contaminated soils (90,000m³)
- Ex-situ Chemical Oxidation (500m³)
- In-situ Air Stripping (1000m²)
- Multi Phase Extraction (4000m²)

There were challenges with regard to odours and VOC emissions from contamination sources in the soils and a new protocol was developed in conjunction with the UK Health Protection Agency (HPA) and Environment Agency for monitoring of these issues. Space was limited on-site and novel ways of installing and operating in-situ systems beneath ex-situ biological treatment beds had to be developed.

The contract was completed within the 104 week programme and on budget. All remediation criteria for soils were met and have been approved by the regulators. The groundwater treatment results are at present with the

UK Environment Agency for approval. The cost of the project was £3.2M (€4.6M). Soil treatment costs were circa £2.8M (€4M) with £0.4M (€0.6M) for groundwater treatment.

Groundwater risk assessment without source term data

J. Dottridge and L. Heaney (Mott MacDonald, Cambridge, UK)

Accidental rupture of a pressurised, underground fuel line at an air base released almost 200 m³ of jet fuel into the ground. The spill occurred at a highly vulnerable location, where thin permeable drift overlies transmissive Lower Chalk with a shallow water table. The site is approximately 2.5 km upgradient of a public water supply. To safeguard water supplies, a rapid risk assessment was required, to predict the breakthrough time at the abstraction borehole and to forecast concentrations with time. Due to lack of access and site specific data, it was also necessary to estimate the source term. Contaminant screening and identification of contaminants of concern (CoCs) were undertaken to forecast the likely maximum concentrations in groundwater beneath the spill area, based on the composition of JP-8, solubility of the major components and Raoult's law. JP-8 contains low concentrations of BTEX but high concentrations of light aromatic fractions. The calculated maximum concentrations were compared to the drinking water standards to identify potential CoCs. A conceptual site model with two alternative interpretations of the hydrogeology was developed and modelling was undertaken using the Environment Agency's Remedial Targets Worksheet model to calculate the likely concentrations of representative compounds at the abstraction borehole. Interpretation of the results suggests that the contamination could reach the abstraction borehole in less than 2 weeks, but only if the major fracture zones are extensive. Higher maximum concentrations were reached by assuming a thicker flow zone in the Chalk, with travel times ranging from 3 months to 10s years, depending on the contaminant. With limited site monitoring data, the model was calibrated and the derived source terms were found to be credible thus minimal revision was required. The simplistic model was then refined using Modflow and MT3D to simulate 2-D flow and reactive transport.

Groundwater modelling of plume rebound around TCE NAPL zone in support of source removal

H. Fraser and W. Wood (ESI Ltd, Shrewsbury, UK)

Soil and groundwater contamination due to releases of trichloroethene (TCE) were detected at an aluminium extrusion works, as were breakdown products of this contaminant. The site is underlain by alluvial sands and gravels, then by Mercia Mudstone. Impacts to local surface waters had been observed.

Contaminant transport modelling was undertaken to simulate migration of contamination from estimated source locations to the current plume distribution over a period of 20 years. Simulation of the plume was completed for a number of scenarios: 1) continuous pump and treat without removal of the source; 2) monitoring of concentrations after the pumps are turned off after two years of pumping; 3) after 3 months pumping, the source is removed by a hypothetical 100% efficient remediation technology and pumping then continued until an asymptote is reached.

These simulations indicated that it is unlikely that significant decreases in groundwater concentrations would occur close to the sources of contamination so long as the contaminant source remains in the ground. Simulation of turning off a hypothetical pump and treat system upon reaching an asymptote when the contaminant source is still present indicated that groundwater contaminant concentrations would rebound to concentrations similar to those prior to pumping. Simulation of a scenario where the contaminant source is removed after three months of pumping, but where the pumping is continued, indicates that significant decreases in concentration can be expected after two to three years. Therefore there would be significant benefits in removing DNAPL contamination if its position could be reliably established.

Source zone characterisation and the influence of aquitard topography on DNAPL distribution

H. Fraser and H. Streetly (ESI Ltd, Shrewsbury, UK)

DNAPL was detected below storage bunds at a site underlain by alluvial sands and gravels and then by a stiff Boulder Clay. Extreme variations in DNAPL concentrations in soil collected from closely spaced samples taken at the site were observed. The concentrations observed in groundwater samples collected from the site were generally less variable than those in soil samples, reflecting the effects of groundwater mixing.

Extensive sampling was undertaken in the source zone at the base of the alluvial materials, and an examination of the influence of aquitard topography on DNAPL distribution made. The site data indicated that aquitard topography could not wholly explain DNAPL distribution; other factors included the spatial distribution

of losses, the heterogeneity of the sediment lithology and the mechanisms controlling the relative distributions of the dissolved and free-phase DNAPL in the subsurface.

Assessment and enhancement of hydrocarbon natural attenuation using biofilms

K. Hampson, S. Kelly and B. Reid (University of East Anglia, UK)

Natural processes can prevent hydrocarbon contaminants reaching water resources. These processes include biodegradation, dilution, diffusion, dispersion, sorption, and volatilization. Of these, regulators favour biodegradation because it removes contaminants from the environment. A remediation strategy that embraces such a process, and then monitors its influence on contaminant movement, is called 'monitored natural attenuation' (MNA).

The objective of this project is to develop a passive sampling device that simulates contaminated groundwater environments to investigate the biodegradation of the herbicide groups; phenyl urea and carbamate. The project will encompass extensive laboratory and field trials. The trials will explore how biodegrading microbes become attached to surrogate aquifer materials, pre-loaded with an isotopic tracer of the contaminant. This tracer will track the contaminants metabolized into the phospholipid bilayer of the microbial cell wall.

Initially the adsorption and desorption kinetics of the surrogate aquifer materials will be investigated using radiolabeled contaminants and Liquid Scintillation Counting (LSC) methods. This will be followed by aerobic and anaerobic microcosm studies using ^{14}C Respirometry and the resultant $^{14}\text{CO}_2$ measured using LSC. A second series of trials will investigate the use of ^{13}C labeled contaminants, instead of ^{14}C and the levels of ^{13}C metabolized determined using Compound Specific Isotope Analysis (CSIA).

Comprehensive field trials will be undertaken in collaboration with two world-class industrial partners. These trials will involve lowering the devices into contaminated boreholes for periods of up to one month, after which the devices will be returned to the laboratory for CSIA analysis.

Once validated, the passive sampling device should prove to be a valuable MNA regulatory tool. In addition, the device will also provide a window into groundwater ecology and offer insights into optimal cost-effective remediation strategies.

Investigating LNAPL drop hysteresis: Implications for residualisation and source zone assessment

J. Heneghan and R.D. Wilson (University of Sheffield, UK)

The wetting behaviour of Light Non-Aqueous Phase Liquids (LNAPLs) is one of several parameters that control their behaviour in the subsurface and influences processes such as invasion, residualisation and free-phase recovery. The NAPL contact angle is typically regarded as the definitive measure of wettability. In studies where contact angle is recorded it is typically measured as a static value. Although this approach has the value of indicating the likely wetting state in the system at equilibrium, it does not provide information on variability in the wetting during imbibition and drainage, processes that control the degree of residualisation. In order to improve understanding of NAPL residualisation and enable the accurate characterisation of contaminant source zones it is suggested that hysteresis of contact angles is a more valuable measurement than static contact angle values. Contact angle hysteresis is defined as the difference in the maximum advancing angle of a drop and its minimum receding angle, thus necessitating the analysis of dynamic drops. As well as observed variation in the contact angles of the static drops, measured values of drop hysteresis have been shown to vary according to the solid surface upon which contact angle is measured. As an example of variation in drop hysteresis water-petrol hysteresis has been measured as $>75^\circ$ on quartz surfaces and $>45^\circ$ on iron oxide (haematite) surfaces. This variation, when related to pore geometry and mineralogy, has potentially significant implications in understanding and modelling the process of residualisation in a given porous media.

The effectiveness of chemical oxidation to remediate DNAPL in fractured porous media evaluated via numerical simulations

TiWee Pang, Jason Gerhard (University of Edinburgh, UK) and Bernard Kueper (Queens University, Canada)

Fractured rock and clay formations represent significant fraction of groundwater aquifers and are highly susceptible to dense, non-aqueous phase liquid (DNAPL) contamination. The goal of this research is to evaluate the effectiveness and benefits of chemical oxidation in remediating DNAPL contaminated fractured porous media environments by using computer modelling. A two-dimensional two-phase flow model is coupled to a non-linear reactive transport model to study the efficiency of potassium permanganate treatment on

DNAPL source removal in various types of rocks. An adaptive gridding routine (AGR) is applied to allow the model to accurately capture dissolved contaminant concentration gradients in the aquifer matrix while still ensuring the overall efficiency of the model. The simulations conducted using the model include examining different types of DNAPL, types of fractured soil, methods of potassium permanganate delivery, changes in mass flux leaving the source zone, changes in diffusive transfer to the matrix and various fracture apertures dimension. This study provides an insight into the key geological physical and chemical parameters that influence DNAPL contamination and the effectiveness of chemical oxidation in fractured rock environments.

Case study of iterative modelling to predict the location and size of an off site chlorinated solvent source zone

M. Plimmer (Geotechnical & Environmental Associates, UK)

Within England and Wales the majority of soil and groundwater contamination tends to be addressed through 'voluntary' action under the planning regime as opposed to being dealt with through primary legislation such as Part IIA of the 1990:EPA. The planning regime is restricted to the boundaries of the application site and so commonly only part of a contaminant plume may be present within the area available for investigation. As access beyond the site boundary is often unavailable or 'politically' sensitive it is often necessary to attempt to characterise a contaminant source zone or down gradient plume from the limited data that can be obtained from within a site's boundaries.

This paper presents a case study of the investigation and modelling of an off site chlorinated solvent source. The groundwater at this former petrol filling station site, located in Birmingham, was found to be contaminated by tetrachloroethene (PCE), trichloroethene (TCE) and dichloroethene (DCE) during remediation validation. The tank removal exercise destroyed the majority of the groundwater monitoring installations hence further standpipes were installed in the limited areas available avoiding the area under construction. A programme of monitoring and permeability testing was carried out to refine the conceptual model of the site and the results were utilised to calibrate a model of the site through an iterative process using ConSim. This modelling suggested a relatively small source located off site on an adjacent laundry, and was sufficient to allow the Planning Condition relating to groundwater contamination to be discharged. The Environment Agency subsequently investigated the laundry site and identified the source of the contamination to be a small zone where a number of drums of solvent waste had been tipped within two metres of that predicted by the modelling.