CL:AIRE

RB 3
(January 2006)

research bulletin

CL:AIRE research bulletins describe specific, practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes research being undertaken at the SIReN site.

Project SIReN: The Site for Innovative Research into Monitored Natural Attenuation

1. INTRODUCTION

This research bulletin aims to provide an update on the concurrent Monitored Natural Attenuation (MNA) research projects being undertaken at the Site for Innovative Research on Natural Attenuation (SIReN) to demonstrate the technical feasibility of this approach.

SIReN is a national initiative for research into MNA, specifically under UK conditions. It is a joint initiative between Shell Global Solutions UK, the Environment Agency for England and Wales (EA), CL:AIRE and AEA Technology. Administration of the SIReN project is funded by Biffaward Landfill Tax Credit Scheme with third party funding from the Energy Institute.

2. SITE BACKGROUND

2.1 SITE LOCATION AND DESCRIPTION

The SIReN research site comprises a large (180 ha) petrochemical manufacturing plant, which has been operational for the past 50 years. The site is located approximately 1 km south-east of a confluence between River A (which bounds the site to the north) and Canal A (which lies approximately 250 m to the west). Currently the site is bordered by other industrial facilities, green belt land, and surface waterways.

Site geology comprises four layers, each varying in thickness across the site:

- Layer 1 (at surface) - Sand and Gravel (2.85-8.5 m);
- Layer 2 - Clay (0.36-30 m);
- Layer 3 - Sand and Gravel (0-7.6 m); and
- Layer 4 – Sherwood Sandstone (Major Aquifer, >77 m).

2.2 CONTAMINANT SOURCES

Initial site characterisation revealed several shallow groundwater plumes in Layer 1, comprising benzene, toluene, ethylbenzene and xylene (BTEX), trimethyl benzenes (TMBs), naphthalene, styrene and trace amounts of other chemicals (Jones *et al.*, 2001; Lethbridge *et al.*, 2002; Swannell *et al.*, 2002). In addition, trace contamination was detected at the top of the deeper Sherwood Sandstone aquifer (Layer 4) in Area C1 (Jones *et al.*, 2001; refer to Figure 1).

Identified source areas include Area B1 (BTEX, butyl-, propyl-, methyl-benzene, and naphthalene), Area C1 (BTEX, styrene, naphthalene) Area C2 (styrene) Area C3 (BTEX and naphthalene), Area C4 (ethylbenzene and styrene) and Area C5 (BTEX, styrene, naphthalene), depicted on Figure 1 (area nomenclature consistent with Jones *et al.*, 2001).

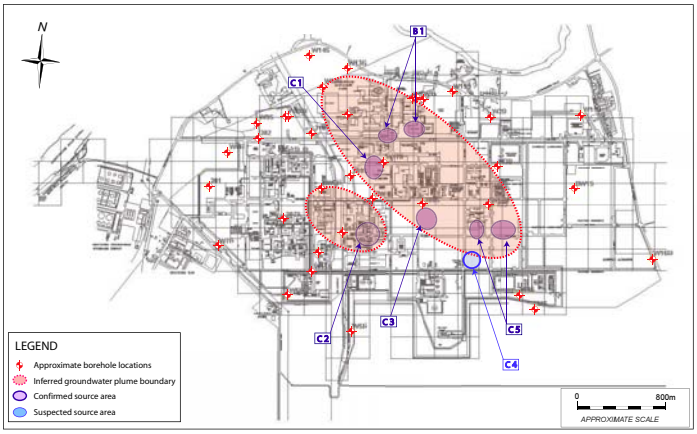


Figure 1. SIReN site layout showing contaminant source areas.

2.3 RECEPTORS

The key potential receptors are determined "controlled waters", which comprise the Sherwood Sandstone Major Aquifer and identified surface water bodies.

2.4 PATHWAYS

Key pathways to the identified receptors were recognised to be through groundwater flow. Regional groundwater flow is towards the north-west and the confluence of River A and Canal A. Locally, in the upper sands and gravels, some deviation from this groundwater flow pattern is dictated by the clay confining layer. A conceptual site model has been developed for the site as illustrated in Figure 2.

3. PROJECT BACKGROUND

3.1 MONITORED NATURAL ATTENUATION

CL:AIRE Site Bulletin SB2 introduced the concept of monitored natural attenuation at SIReN. It is not the intention to reproduce this discussion here and the reader, if unfamiliar with the natural processes which can mitigate potential environmental and human health risks, is directed to CL:AIRE to obtain a copy of the relevant bulletin (www.claire.co.uk).

3.2 PROJECT SIReN OBJECTIVES

The SIReN project's technical objectives are to:

- Provide a well-characterised site for co-ordinated MNA research;
- Contribute towards defining the operating window for MNA in UK hydrogeology; and
- Develop a cost-effective MNA strategy for "mega" sites addressing the challenges of multiple sources and co-mingled plumes.

CL:AIRE research bulletin

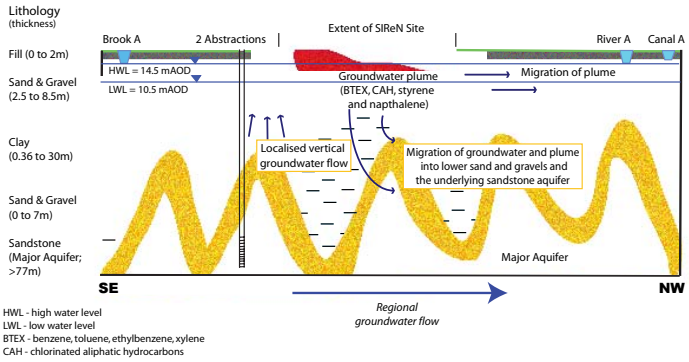


Figure 2. Schematic conceptual site model.

4. RESEARCH PROJECTS AT SIReN

A number of research projects are ongoing at the SIReN site, covering a broad range of themes: 'smart' monitoring/site investigation, decision-making tools for MNA, and specific remediation technologies.

In addition to the characterisation of the site, a number of research projects began during 2003. Among the 12 research projects on site over the past year, three major projects are discussed below.

4.1 CURRENT PROJECTS - AN UPDATE

4.1.1 Decision-Making Tools for MNA: An *In Situ* Aquifer Assessment Tool (University of Sheffield)

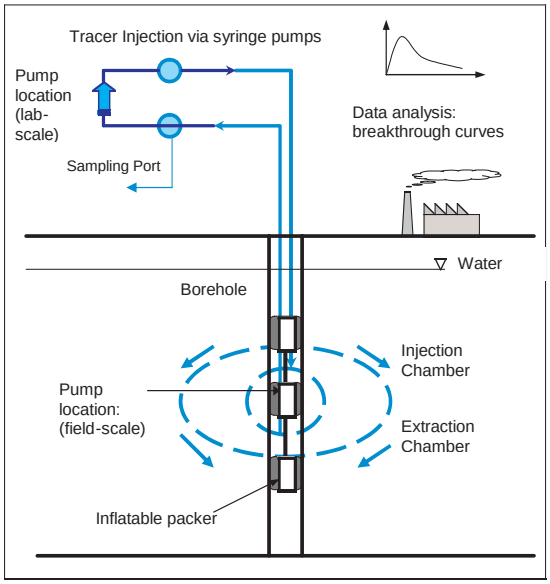
This is a FIRSTFARADAY project led by the University of Sheffield. The project objective is to develop a dipole flow reactive tracer test (DFRTT) to improve the risk-based assessment and remediation of contaminated land by MNA that will inform future risk assessment programmes. The DFRTT is a method that induces a "dipole-flow" in the aquifer by pumping water into an injection chamber and out of an extraction chamber within a groundwater well whilst the chambers are isolated from the rest of the well using inflatable packers (Figure 3). It aims to allow for reliable, rapid and cost-effective 3D determination of aquifer hydraulic, geochemical and biodegradation properties, thereby providing better understanding of contaminant plume behaviour.

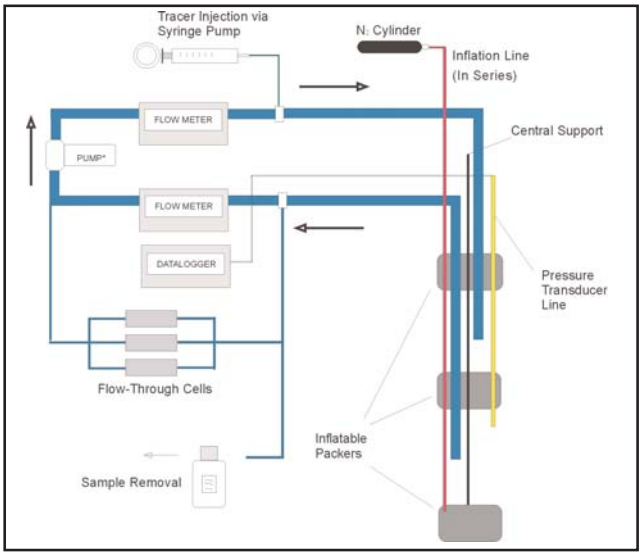
The ultimate aim of the project is to incorporate the three critical system components – steady-state groundwater flow, aqueous phase reactive transport and the reactive solid phase – into a single numerical model using the minimum number of field tests, thus facilitating the use of the DFRTT as a powerful and predictive site assessment tool.

Outcomes:

- Hydraulic parameters have been determined from pumping tests at various depths in boreholes.
- Basic reactive properties have been determined from analysis of recovered aquifer core.
- Rigorous field trials have been conducted at SIReN which demonstrate the DFRTT's potential as an Aquifer Assessment Tool for MNA:
  - Hydraulic data indicates successful establishment of a dipole flow field; and
  - DFRTT shows capability to allow for the injection and recovery of chemical tracers.
- A lab-scale aquifer has been constructed with functional testing underway. Design of scaled DFRTT probe and tracer injection/recovery system is complete with commissioning tests being designed and assembly of the probe being undertaken for the start of tests at lab scale.
- A new model calibrated using site-specific data to replicate field tracer breakthrough curves. The model has been demonstrated to reliably simulate the field breakthrough curves and is to be developed further following laboratory and further field trials.

Led by the University of Sheffield, the project team includes the University of Nottingham and Queen's University Belfast, Shell Global Solutions UK, BP, Environment Agency of England & Wales and SecondSite Property Holdings (now





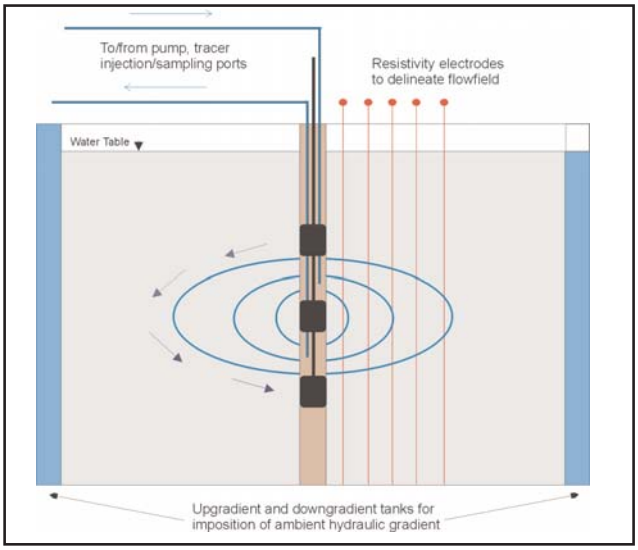


Figure 3. A conceptual model of the dipole flow and reactive tracer test (top). A schematic diagram of the dipole probe assembly (middle). A cutaway diagram of the sandbox aquifer model with the dipole located at its centre (bottom).

National Grid Property). For more information contact Prof Steve Banwart (S.A.Banwart@Sheffield.ac.uk).

Within this project, EPSRC PhD student Chris Berryman, supported by an industrial CASE award from CL:AIRE/AEAT, is developing a sandbox-scale aquifer model to demonstrate the DFRTT under controlled laboratory conditions (see Fig.3). The sandbox is constructed from welded high density polyethylene (HDPE) to form a box open at the top that is 2m by 2m and 1.2m in depth. Packing of the sandbox is with graded Permio-Triassic sand that is unwashed and retains its original clay content. This allows for the laboratory facility to approximately replicate the SIReN aquifer geochemical properties.

Over the forthcoming 12 months, experimentation is to progress in the sandbox facility using inert and reactive tracer tests. If reactive tracers can be successfully demonstrated using the sandbox facility to assess NA processes, similar experimentation will then be trialled at the field site. Field trials would aim to offer evidence to demonstrate the performance of NA processes in the SIReN aquifer and demonstrate the potential of the DFRTT as an Aquifer Assessment Tool (AAT) to support a MNA strategy at contaminated sites.

4.1.2 An Integrated Strategy for Monitoring Natural Attenuation Using Chemical Fingerprinting and Molecular Analysis (ISMoNACh; University of Essex)

This LINK bioremediation project is developing a strategy for monitoring natural attenuation of benzene-contaminated groundwater using chemical fingerprinting and molecular analysis. The overall objective is to investigate the factors affecting benzene degradation and determine the associated microbial communities.

Small (centimetre-scale) mini-arrays of sensors were used to generate time profiles of fingerprint changes in the chemical environment during benzene degradation, whilst the role of microbial communities involved in benzene degradation was analysed using stable isotope DNA probes. Spatial heterogeneity of benzene degradation and associated microbial communities involved in benzene degradation are then correlated with available geochemical and hydrgeochemical data.

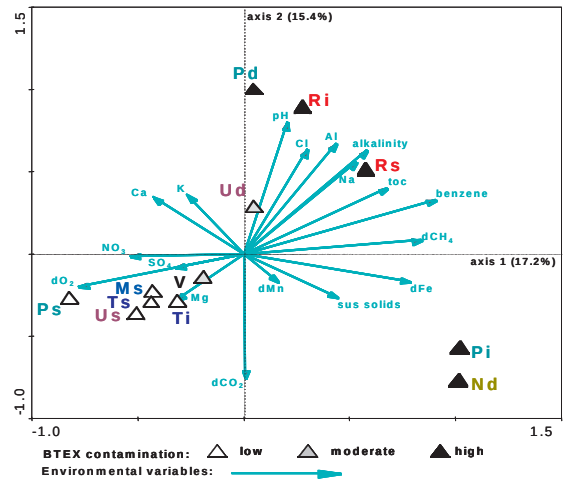
These techniques are combined with novel micro-membrane headspace/sample extraction probes to allow *in situ* monitoring of chemical profiles with minimal microenvironment disturbance together with periodic sampling of benzene-degrading microbes.

Outcomes:

The work discussed below was published in full in Environmental Microbiology earlier this year and although summarised here, the reader is referred to the full paper for the complete details.

- In groundwaters contaminated with more than 1.8×10^4 µg/l of benzene, the long term presence of benzene was found to halve bacterial diversity;
- Terminal restriction fragment length polymorphism (T-RFLP) analysis of 16S rDNA revealed that clean groundwaters have similar bacterial communities to each other;
- Bacterial communities subjected to long-term benzene contamination were different, not only from uncontaminated groundwater communities, but also from each other; and
- This divergence was primarily caused by changes in environmental conditions (anoxia) brought about by benzene metabolism, rather than direct toxic or stressful effects of benzene, in particular a decrease in redox potential.

Figure 4 shows canonical correspondence analyses of the bacterial community T-RFLP profiles combined with the groundwater geochemistry. Clean wells form a tight cluster, whilst contaminated wells are distinct from each other. Although benzene accounts for most of the variance amongst the geochemical parameters, its importance with respect to the community structures is on par with Al, TOC, O_2, pH, CH_4, and alkalinity.



Notes:

toc = total organic carbon; sus solids = suspended solids; d = dissolved; M, N, P, R, T, U, V represent the wells locations; the relative depth is indicated by s (shallow), i (intermediate) and d (deep).

The wells are represented by triangles shaded according to their level of benzene contamination (clean = white, low = grey, high = black), and the environmental parameters by arrows. The distance between the wells reflects their dissimilarity, and their position in relation to the arrow heads is a function of the influence of that specific parameter on the well. The angles between arrows illustrate the correlations between the parameters: arrows in similar or opposite directions respectively denote a positive or negative correlation, and arrows placed at 90 indicate a close-to-nil correlation. The length of the arrows is a function of the relative effects of the environmental parameters. The position of the environmental parameters is determined solely by their influence on the community structures.

Together, axes 1 and 2 account for 32.6% of the variability.

Figure 4. Relationship between community T-RFLP profiles and geochemical analyses.

Led by the University of Essex, the project team includes Birkbeck College, Quartz Technology and Shell Global Solutions. For more information contact Anne Fahy (afahy@essex.ac.uk) or Terry McGenity (tjmcgen@essex.ac.uk).

4.1.3 ROTAS™ – A BIO-WISE Demonstration Project (Cybersense Biosystems Ltd)

SIReN is a flagship field site for Cybersense Biosystems Ltd's ROTAS™ project. ROTAS™ (Rapid On-site Toxicity Audit System) is a portable biosensor that allows rapid, on-site toxicity testing of contaminated land and water.

The system was developed to give additional information to complement chemical analyses, and to help save money on analytical costs by more effectively targeting sampling and analysis for a range of contaminants and contaminated media.

The ROTAS™ system uses naturally occurring, bioluminescent bacteria that emit varying degrees of light depending on the toxicity of their surroundings. Extracts of soil samples are mixed with the biosensor reagent and the change in light output is recorded by a ROTAS™ luminometer and subsequently analysed by specially developed software.

A series of field tests were carried out at SIReN and other sites in the UK and overseas in which analyses using ROTAS™ were compared with and calibrated against chemical/Ecotox analyses. These facilitated an in depth demonstration and comparison of biosensor toxicity with chemical and ecotoxicity analysis.

The SIReN site trials showed a good correlation (>80%) indicating that the ROTAS™ assay can be used to rapidly screen for BTEX compounds in groundwater as measured by their acute toxicity.

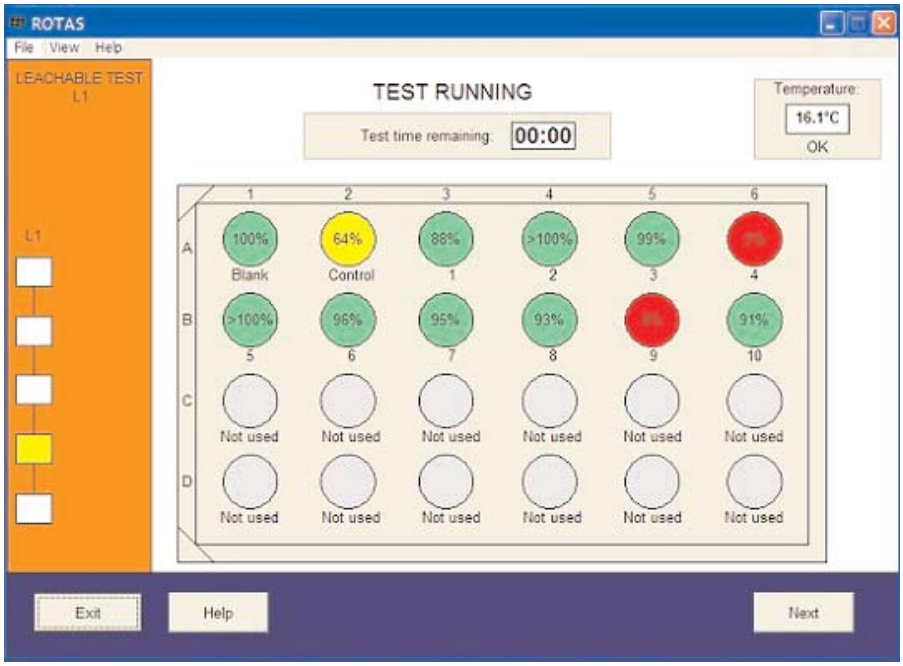


Figure 5. Example ROTAS™ interface screen (above); the portable ROTAS™ biosensor (top right); ROTAS™ at work (bottom right).

Cybersense's ROTAS™ project was completed in 2003. The ROTAS™ system was launched commercially in April 2004 and is now in use in the UK, Italy, Sweden, South Africa and Japan. The system was recently used on a remediation of a former oil refinery, where over 8,000 ROTAS™ samples were taken to assist with the delineation of the contamination, stockpile management and site validation.

The ROTAS™ project is a DTI BIO-WISE Demonstration project. For more information contact Dr Tim Hart at Cybersense Biosystems Ltd (tim@cysense.com).

4.2. SUMMARY

MNA has considerable potential to sustainably treat contamination *in situ*, reducing the amount of material requiring *ex situ* treatment or disposal to landfill. As such, MNA can be a cost-effective risk management remedial tool alternative to more traditional engineering options. Given the difficulties and costs inherent in many site remediation settings, MNA may on occasion be the only technically feasible option.

The ongoing research projects at SIReN have developed strategies to demonstrate MNA at large complex sites with multiple sources with co-mingled plumes. The third CL:AIRE bulletin will describe the lessons learnt and put the future of MNA in the UK into context.

4.3 COMPLETED PROJECTS

Additional projects have included a number of MSc and PhD projects utilising samples obtained from the site during the ongoing site characterisation. Findings from all research projects can be found at www.claire.co.uk/siren.php.

SIReN based projects completed thus far include the following:

- Analysis of the microbial ecology of the site (Anne Fahy, Terry McGenity, Andrew Ball and Ken Timmis, University of Essex); also "Bacterial Diversity and community dynamics in a benzene-contaminated sandstone aquifer" Anne Fahy (PhD Thesis, 2003).
- Investigation into methods for speciating iron in the Groundwater (MSc student supervised by Simon Bottrell, University of Leeds);
- Monitored Natural Attenuation (MNA): Application of the Environment Agency (for England and Wales) MNA Guidance to the SIReN Site - Angela Sheffield (MSc Thesis, 2001), Nottingham Trent University.
- Variability of cation exchange capacity beneath the Site for Innovative Research in Natural Attenuation - Robert Michael Smith (MSc Thesis, 2003), University of Reading, Post Graduate Research Institute for Sedimentology.
- Predictive Modelling of Organic Contaminant Migration at a Petro-Chemical Site - Daniel Bentiez Galvez (MSc Thesis, 2001), Imperial College of Science, Technology and Medicine, University of London.

5. REFERENCES & OTHER PUBLICATIONS

BBSRC. 1999. A Joint Research Council Review of Bioremediation Research in the United Kingdom. BBSRC, Swindon, UK.
DETR. 2001. Audit of Contaminated Land Research in the UK. DETR, London, UK.
Fahy, A., Lethbridge, G., Earle, R., Ball, AS., Timmis, KN., and McGenity, TJ. 2005 Effects of long-term benzene pollution on bacterial diversity and community structure in groundwater. Environmental Microbiology, v7 Iss8 pp. 1192.
Jones, D., Lethbridge, G., McCarthy, P., & Thomson, S. 2001. Project SIReN: Phase 2a Conceptual Site Model & Groundwater Model. R&D Technical Report P2-208/TR/2, Environment Agency, UK.
Lethbridge, G., Scott, P., & Earle, R. 2002. Project SIReN Phase 2b. Further Investigation (Phase 2b) of the SIReN (Site for Innovative Research on Natural Attenuation) Site. R&D Technical Report P2-208/TR/3, Environment Agency, UK.
Swannell, R., Macnaughton, S.J., Lethbridge, G.L., Neaville, C., and Hart, A. 2002. SIReN: the site for innovative research into monitored natural attenuation. Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution Proceedings of the Groundwater Quality 2001, IAHS Publication 275, pp. 97-99.

ENVIRONMENT AGENCY PUBLICATIONS

Project SIREN: Phase 1 Report. Environment Agency 2000. R &D Technical Report P358, Environment Agency, UK.
Project SIREN: Benchmarking of Monitored Natural Attenuation Procedures. Environment Agency 2001. R&D Technical Report P2-208/TR/1, Environment Agency, UK.
Project SIREN: Conceptual Site Model. Environment Agency 2001. R&D Technical Report P2-208/TR/2, Environment Agency, UK.
Project SIReN: Phase 2b. Further Investigation (Phase 2b) of the SIReN (Site for Innovative Research on Natural Attenuation) Site. R&D Technical Report P2-208/TR/3, Environment Agency, UK.

For further information and contact details please visit the SIReN website at www.claire.co.uk/siren.php