case study bulletin

CL:AIRE case study bulletins provide a source of information on the characterisation and remediation of specific sites in the UK. This case study bulletin describes the laboratory and field evaluation of a biological permeable reactive barrier for remediating organic contaminants in soil and groundwater. The field site was located in Portadown, Northern Ireland.

Laboratory and Field Evaluation of a Biological Permeable Reactive Barrier for Remediation of Organic Contaminants in Soil and Groundwater

1. INTRODUCTION

Risk-based remediation requires knowledge to best manage our industrial legacy using source treatment, boundary interception techniques, or plume management. Many sites throughout the world are contaminated with potentially harmful and complex mixtures of organic compounds. Traditionally, source treatments mainly rely on *ex situ* clean up that involves excavating the contamination and disposing it in landfills, or chemically/biologically treating it. However, the large costs involved (both in the UK and other countries) and a world-wide move towards more sustainable remedial technologies has prompted developers to consider alternative *in situ* methods of dealing with contaminants. Some of the most promising alternative technologies are based on the biological degradation of contaminants. Natural attenuation (NA) has received significant attention in the last decade. Monitored natural attenuation (MNA) is used for risk management of contaminant plumes. However, application of MNA is at times limited, and there can be high risks associated with contaminant movement that limits the potential to use MNA.

Permeable reactive barriers (PRBs) are a passive intervention remediation technology. In PRB systems contaminated groundwater passes through an *in situ* reactive material that either biotically or abiotically degrades the contaminants. PRBs are unique because they can be inserted to prevent contaminant movement across site boundaries prior to risk receptors, or simply to intercept a contaminant plume. Barriers of zero valent iron have been shown to abiotically degrade chlorinated solvents. One such reactive iron barrier, located in Northern Ireland, was linked to this project and has also been published as a CL:AIRE technology demonstration project report (TDP3). However, zero valent iron is incapable of degrading organic contaminants such as polycyclic compounds and fuel-derived hydrocarbons. PRBs using activated carbon can remove many organic contaminants from groundwater through sorption (non-destructive process), but destruction of the sorbed contaminants is still required. Biological systems have the potential to degrade a wider range of contaminants, therefore a research project was designed to study how a biological PRB could be used to not only degrade organic contaminants but also to be self-sustainable over years to decades.

This Case Study Bulletin describes the research project which evaluated, at laboratory -scale and field-scale, a biological PRB for remediating organic contaminants.

A small, former gas works site (15,000 m^2) in Portadown, Northern Ireland was made available by McCallan Bros. Ltd to undertake this EPSRC WPM research. A linked research grant funded by the DoE Northern Ireland was used to design and install infrastructure for a modular reactive barrier. The joint DOE - EPSRC research project required site study (trial pits, boreholes, chemistry, hydrogeology and microbiology), risk assessment, formal planning permission, regulatory agreement, discharge consents, laboratory treatability for full-scale design, hydrogeologic and civil engineering design, modelling and finally construction of a full-scale PRB including 330 m of slurry wall (to 13 m depth) and the 20 m^3 reactor. Professor Robert Kalin acted as Project Manager and his research group at Queen's University Belfast, in the School of Civil Engineering, acted as Main Contractor for all works on site.

Figure 1: Laboratory-scale experimental set-up.

2. AIMS AND OBJECTIVES OF THE PROJECT

The aims of the research were:

1. To understand how temporal variation of hydrogeological and geochemical parameters affect the long term performance of a laboratory and field-scale biological PRB.

2. To understand the balance between hydrodynamic flux, microbial metabolism and biofilm development within laboratory and field-scale biological PRB.

3. Link aims 1 and 2 within a biogeochemical model of the site to study the performance of the biological PRB and to help optimise future operating conditions.

4. Evaluation of the overall performance and expectations of biological PRBs for contaminated land and groundwater risk management and contrast with current accepted PRB methods in the UK and Europe.

5. Draft a document, in collaboration with industry partners, on the design, performance and monitoring criteria for the future application of biological PRBs.

To meet these aims the project gained real-life field experience in the design, installation and performance of the biological PRB. In collaboration with industry partners, experience and knowledge from the EPSRC project was used to produce an Environment Agency (EA) document: Guidance on the use of permeable reactive barriers for remediating contaminated groundwater (EA, 2003).

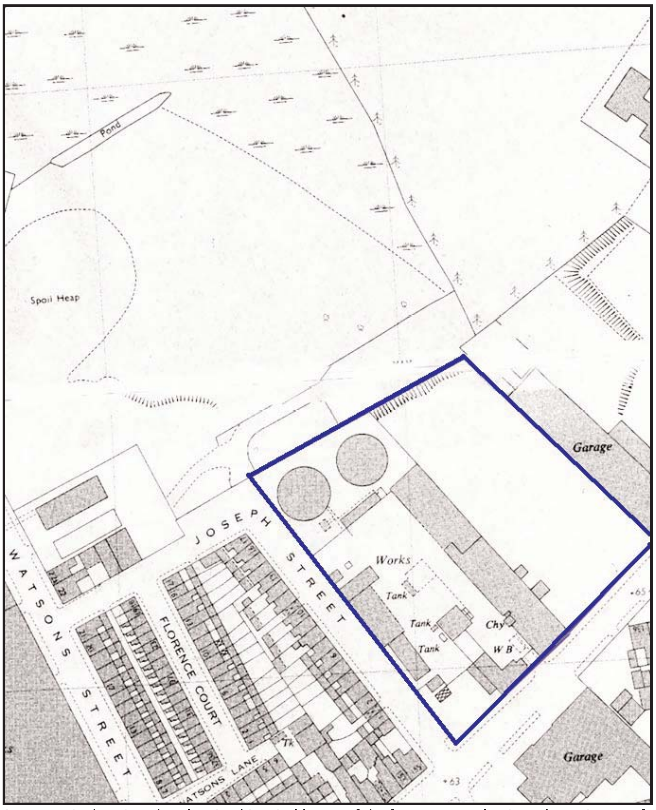

Figure 2: Site location plan showing historical layout of the former gasworks site. The perimeter of the site is indicated by a blue boundary line.

3. SITE LOCATION AND DESCRIPTION

The site is located in Portadown, Northern Ireland, at 165 Bridge Street, Ordnance Survey [200NE, 543-016] (Figure 2). Bridge Street and Joseph Street border the site on its southern and western sides. Joseph Street is a residential area whereas Bridge Street is a main thoroughfare of the town. The site is bordered on the northern side by a spoil heap. Dumping of material is thought to have continued here to the present day. The spoil heap overlies an area of 'wetlands' which continues northwards towards the M12 motorway. A car dealership with servicing department is located directly south of the former gasworks on Bridge Street. There is a petrol station to the east of the site.

The majority of above ground structures on the site have been demolished, foundations of buildings are still thought to be present, and these may include underground tanks, interceptors, the bases of the gasholders, and associated pipework. Two gas holding tanks are located in the northern end of the site, and the purifiers and store were located at the western side of the site adjacent to Joseph Street. A tar well is situated in the centre of the site and has been backfilled with demolition rubble. A north-south running ballast wall exists in the centre of the site, and surface water collects on the eastern side of this wall.

The site generally dips in a south-north direction, generally following the local topography. The wetlands to the north of the site are part of the floodplain of the River Bann, lying approximately 14 m Above Ordnance Datum (AOD); the southern side of the site at Bridge Street is 19.5 m AOD.

4. SITE ASSESSMENT AND SITE CHEMISTRY

The aim of the site work was to gather soil and groundwater geochemistry and hydrogeological data from 44 trial pits sampled at various depths and eight multilevel boreholes, and then develop models that allowed for the design and implementation of a biologic permeable reactive barrier. The investigation approach and conceptual model development is transferable to other similar sites around the UK. The work considered the regional through to site-specific scale hydrogeology and geology refining all available information. The contaminant biogeochemistry and possible biodegradation was also considered. The risk-assessment evaluation identified that within an 81 km^2 area of the Upper Bann catchment in the vicinity of Portadown a vulnerable class A down-faulted aquifer of Sherwood Sandstone occurs at depth. The aquifer was not susceptible to contamination from surface and was also not prone to recharge except through fault planes at either side of the graben. The Glacial Till was identified as a relatively impermeable seal overlying the solid geology and points to contaminant transport in recent sediments within the Upper Bann Valley as the predominant pathway for the migration of contamination. Refining the local system (km^2) around the area of the gasworks site, individual recent lithologies were identified and the water table interpolated. The lithologies and their depositional environments were further refined by site-specific investigation work. Perched water in ash and clinker fill overlying a clay reflector was identified by a geophysics conductivity survey and confirmed by trial pitting. Geophysics and trial pitting also confirmed the presence of foundations and pipe work within made ground across the site.

Evaluation of the natural processes of biodegradation and the biogeochemistry of soil and groundwater at the site showed the redox geochemistry within the area of borehole eight (BH8) and the centre of the site is dominated by the contaminants ammonia (NH_4^+) within the aquifers and sulphate (SO_4^{2-}) within aquitards. Sulphate and methanogenic reducing environments were hypothesised to play a major part in the microbial activity of the groundwater at the site as anoxic conditions quickly increase with depth in areas of contamination. This suggests that aerobic conditions close to the surface quickly become anaerobic within a nitrogen-reduced environment. However, biogeochemical results showed that sulphate does not undergo microbial reduction but acts in a conservative manner. This was then hypothesised to occur due to the presence of ammonium contamination inhibiting biodegradation and keeping redox potentials too high for sulphate reduction too occur (later confirmed through microbial activity research). The fact that redox levels are lower in aquitards than aquifers points also to the influx of groundwater with higher redox potentials.

5. LABORATORY FEASIBILITY STUDY

A laboratory feasibility study for the PRB, using a 2-D pilot scale reactor, was started at the beginning of the project, and was used to determine design criteria for the full-scale PRB reactor. The groundwater used within the feasibility study was collected from the on site sampling point which demonstrated highest concentrations of target contaminants from previous site investigations. The expected reduction in concentration was determined following a period of bioremediation within the laboratory-scale reactor. The priority compounds account for 14.2 mg/L (34 %) of the total organic carbon (TOC) content (41 mg/L). As an approximate method of determining biodegradable TOC, the chemical oxygen demand (COD) was proportioned with the biological oxygen demand (BOD) and compared with the TOC. In the laboratory-scale system there was an 11 mg/L reduction in TOC, close to the biodegradable content. It was assumed the biodegradable TOC was in the range of 12 mg/L - 15 mg/L so a design half-life of 49.5 hours was calculated. Therefore, complete removal of biodegradable TOC was calculated to be achieved with a residence time of 297 hours. The degradation of the BTEXs was measured showing 100 % degradation at time 56.6 hours. The BTEX compounds account for 20.2 % of the total priority compounds. Calculations for biodegradation oxygen requirements were determined using toluene equivalents. The stoichiometric relationship for the biodegradation of toluene is:

$$C_7H_8 + 9O_2 \text{ -------> } 7CO_2 + 4H_2O$$

Therefore the complete mineralisation of toluene requires approximately 3 mg/L of O_2 for each mg/L of TOC.

The TOC content of site water was 41 mg/L therefore the volume of air required is 0.460 L of air per L of groundwater. A back-up study was undertaken that used granular activated carbon (GAC) to sorb any contaminants that did not biodegrade within the reactor. Laboratory column studies showed a design half-life for TOC from Portadown was 1.6 hours. Sorption of TOC from TP11 to the detection limit (1-4 mg/L) was calculated at 6.3 hours. The average TOC concentration for BH7 and BH8 was found to be 93 mg/L. It would take a residence time of 11 hours to sorb 93 mg/L to the detection limit.

The results of these studies allowed design criteria to be produced showing that the permeable reactive barrier should consist of an air sparged bioreactor and GAC reactor placed in sequence with a pea-gravel mixing zone pre- and post- the reactive cell.

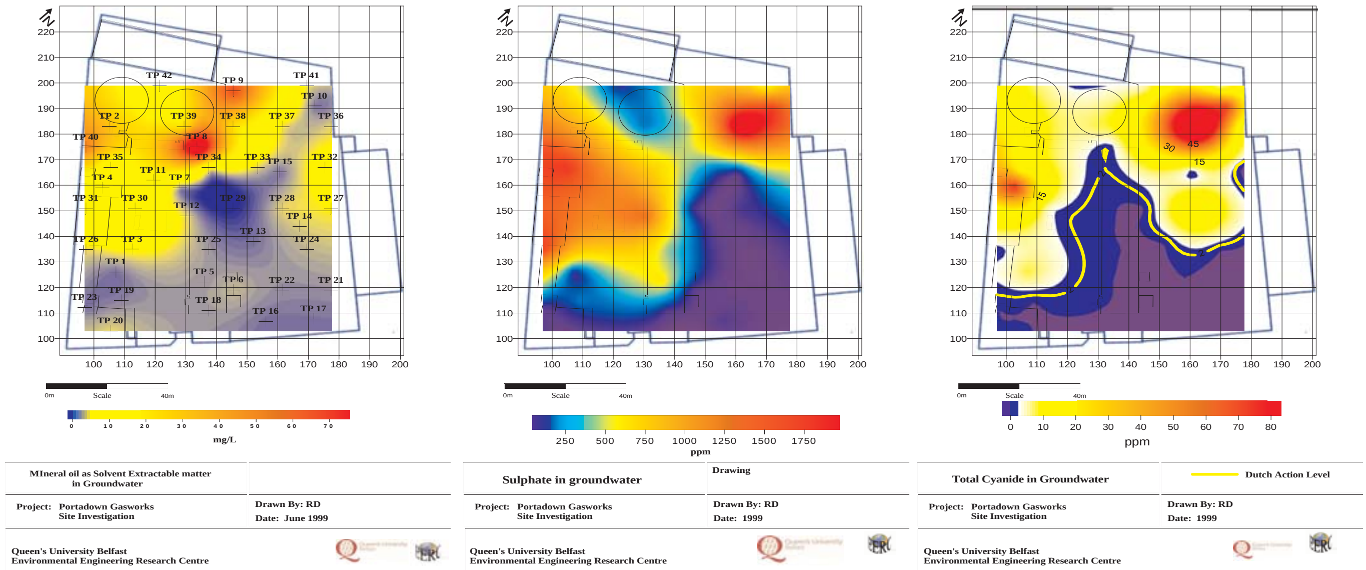

Figure 3: Distribution of groundwater contamination across the site: organics (left), sulphate (middle) and total cyanide (right).

The interpretation of biogeochemical results suggested the microbial research for a biological permeable reactive barrier used at this or within any gasworks site with an ammonium plume should at least focus on the problem of ammonium contamination that may have an effect on degradation of contaminants such as phenols and cresols. The biological PRB was designed to rely on an aerobic environment to degrade organic matter where ammonium is fully oxidised until organic matter is preferentially degraded.

6. MODELLING AND STATISTICS

A detailed groundwater flow and contaminant reactive transport model was produced to both evaluate the risk at the site and as a basis for predictive modelling of the proposed biologic PRB. Manual calibration was refined with automated parameter estimation that successfully calibrated site-specific groundwater simulations. Contaminant transport modelling of organic contaminants with various distribution coefficients confirmed that the majority of dissolved organic contamination is likely to have originated from a single source in the area of the tar well. Contaminant transport modelling suggests that a boundary interception PRB risk-based remediation of lighter dissolved aromatic organic contaminants was necessary to manage risk of off-site migration of the plume. The reactive cell of the PRB should be constructed at the site perimeter in the centre of the contaminant plume (design requirement). The contaminants with higher distribution coefficients occur within lower and upper aquifers close to the source area of the tar well. Contaminants with lower distribution coefficients (benzene, naphthalene) occur mainly within the lower aquifers but did occur close to surface further away from the source area. Vertical dispersivity and time play an important role in the spatial discretisation of organic contaminants from a single source.

A novel statistical site investigation method was developed that reduces the number of intrusive data points needed to carry out site investigation - Quadrant Validation with Acceptable Error (QVAE), (Doherty *et al.*, 2001a). Once the slurry wall was installed, it was decided to evaluate the hydrogeologic response of the aquifer prior to installation of the reactor. The groundwater model provided an initial assessment of the hydraulic performance of the slurry wall. Discrepancies between observed and modelled head recovery upstream of the slurry wall indicated minor flow into the Glacial Till. Continuous monitoring allowed confidence to be gained in the validity of the numerical groundwater flow model, previously calibrated to non-works affected conditions (Doherty *et al.*, 2001b).

7. FIELD-SCALE STUDY

After construction of the reactor in late 2001 (called PRB1) the system was initiated. However, a significant rainfall event occurred during which the HDPE liner of the reactor was torn. The next 9 months was spent working with a sub-optimal water flow through the reactor until October 2002 when the reactor was opened and the sand sub-sampled for microbial activity. At this time the reactor was re-designed (and renamed PRB2) and the failings of PRB1 (mainly the sealing with HDPE and the air sparge units) were corrected. Upon completion of PRB2 the hydraulics showed a good response until early 2003 when it became obvious that the outlet pipe had clogged. Remedial works were undertaken in May 2003 and the reactor hydraulics again worked without problems. The new air-sparging system was scheduled to be turned on in July 2003 when a water main break off-site flooded the surrounding area and reversed the hydraulic gradient into the reactor from off-site. After the water main was fixed, the reactor again ran smoothly and the new air-sparging system was turned on in October 2003.

8. MICROBIOLOGICAL STUDY

The microbiological study was undertaken by Dr Mike Larkin's group in the Queen's University Environmental Science and Technology Research (QUESTOR) Centre. The aims of this study were to i) provide a "baseline" picture of the microbial community at the site - particularly with regard to biodegradation of pollutants and ii) determine the potential effectiveness of the indigenous biodegradative microflora in mediating decontamination of the groundwater pollutants in the proposed biological reactive barrier. Preliminary flask enrichments and laboratory-scale experiments indicated that aerobic heterotrophs were likely to be the main mediators of biodegradation in the reactive barrier. The total cultivatable aerobic heterotrophic microbial counts for subsurface soil samples varied from 4.5 x 10^5 to 8.0 x 10^7 colony forming units (cfu)/g dry soil across the site. Naphthalene and phenol degraders represented 0.74 % and 2.33 % of the total viable cell counts, respectively, although when thiocyanate was used as the sole source of nitrogen these numbers were lower at 0.17 % and 0.46 %. In comparison with soil counts, lower microbial numbers were observed within the planktonic zone (1.13 x 10^5 to 3.76 x 10^6 cfu/ml). It was concluded that there was generally a microbial population of heterotrophic microorganisms capable of biodegrading many of the priority contaminants characterised within the contaminated plume. Changes in the microbial community structure across the site were monitored by 16srDNA cloning and sequencing analysis of soil and groundwater samples and extensive 16srDNA Thermal Gradient Gel Electrophoresis (TGGE) analysis. The latter technique provided a rapid picture of the diversity of 16srDNA sequence diversity (and by inference, microbial species diversity) in individual samples as a series of bands on a gradient gel. This provided a convenient "base-line" assessment of the diversity of the microbial communities at the site. Analysis using restriction fragment length polymorphism (RFLP) was initially used but found to be inconsistent and slow in comparison and was not continued. In general the results revealed an increase in biodiversity in conjunction with increasing contamination levels, before toxicity appeared to become a factor and this was attributed to the accessibility of a wide range of utilisable carbon substrates. The toxicity of samples from the site was also assessed by using the standard Microtox methodology. It was also concluded that this approach provided a convenient "base-line" measurement for the site and can be used to corroborate effective progress in the remediation and quality of the remediated water leaving the site.

8.1 Laboratory-scale studies and on-site studies to assess the effectiveness of microbiological processes

Initial results indicated that a reactive barrier that encouraged growth of aerobic heterotrophic bacteria would be likely to bring about the degradation of many of the pollutants identified. However, it was deemed necessary to carry out trials of a laboratory-scale model based as closely as possible, in relation to hydraulic retention time and size, on a design that could be installed at the site. The previous laboratory model of the proposed PRB was monitored microbiologically, chemically and toxicologically over a considerable time. The laboratory model system was fed via an inlet with site groundwater (extracted at intervals from monitoring point TP11) at a rate of 3.75 l/day. This flow rate was chosen to reflect site conditions. Initial trials of this system indicated that many of the major organic contaminants were degraded within the first 10 % - 20 % of the length of the laboratory reactor. Sand from the reactor was shown to be colonised by a large number of bacteria (near the inlet more than 10^9 bacteria/ml). In a series of tests, both matrix and water samples indicated biodegradation activity for a complex mixture in various concentrations. Biodegradation half lives were under one day for benzene, toluene, naphthalene, phenols and ethylbenzene; p-xylene and o-xylene exhibited longer half lives. However, all compounds tested were degraded below detection limits at the outlet of the laboratory reactor. With regard to available electron acceptors, no change in sulphate composition was observed despite probably anoxic zones associated with biofilms. The high concentration of ammonium ions noted in the groundwater at the site is a contributing factor influencing biodegradation. However, ammonium ions were efficiently oxidised with a concomitant increase in nitrate indicating a healthy population of ammonia oxidisers. These results were confirmed by polymerase chain reaction experiments with specific primers and a potential nitrification activity of 0.049 µM NO_3^-/h/g dw (equivalent to 818 ammonium degraders per g of soil). The $^{12/13}C$ isotope ratio of the total inorganic carbon was significantly increased at the outlet of the laboratory-scale reactor and is consistent with a biological degradation process occurring. The toxicity of the water from the reactor was consistently low after an initial colonisation period. Analysis of the microbial community structure using TGGE of 16SrDNA amplicons showed that the laboratory-scale reactor was colonised by a stable population of bacteria, which had a similar profile to the biofilm found on site during the excavation of the barrier. The groundwater from different sampling points within the full-scale field PRB was similarly shown to harbour a significant number of heterotrophic bacteria (10^6 bacteria/ml), which were able to utilise and degrade a mixture of pollutants at a similar rate to the laboratory reactor populations. Also it was noted in a series of experiments that these microbial populations remained active after two weeks of water saturation at the PRB; where more anoxic conditions would be expected to prevail. It was generally concluded that monitoring of the PRB should continue to assess how the population changes – particularly with respect to ammonium oxidation and ability to degrade key pollutants.

9. RECOMMENDATIONS FOR FUTURE ASSESSMENT OF PRB

A monitoring plan was produced where a series of 20 monitoring points within and external to the field PRB reactor were instrumented with automated logging equipment that measures hydraulic and key chemical parameters (dissolved O_2, E_H, conductivity). These automated measurements confirmed the hydraulic design and operation of the PRB. Microbial assessment should consider physiochemical analysis to indicate the range and potential toxicity of organic pollutants and importantly the inorganic ions likely to influence the physiology of the microorganisms. This includes identifying the key electron acceptors and other key influences such as ammonium concentration. The initial survey should clearly demonstrate that there is a microbial population able to degrade the pollutants and also take into account the potential toxicity of the pollutant plume.

Laboratory-scale trials are essential to determine if the process is likely to work in the field. A new Environment Agency Guidance on Laboratory Treatability Studies has been written by staff in Prof. Kalin's research group and will be published during 2005. The laboratory studies should seek to identify a number of key parameters that are likely to be good indicators for monitoring the effectiveness of the PRB when it is running in the long term; toxicity measurements were identified as convenient and useful. In addition, measurements on key organic contaminants and inorganic ions were found to be highly effective (e.g. monitoring rates of ammonium oxidation and nitrate production). TGGE analyses can provide a good comparative indication regarding the structure of the microbial population and should be periodically checked against other more rapid means to profile the population. DNA samples (DNA microarrays) could be used to give increased confidence and validation.

Figure 4: Field-scale biological PRB

10. RESEARCH IMPACT AND BENEFITS TO SOCIETY

The results of this research were expected to underpin the potential application of biological PRBs to a wide range of contaminants found in contaminated land sites in the UK (e.g. PAHs, BTEX, MTBE). The results of this study were specifically used to help refine the level (i.e. cost) of microbiological and biogeochemical site investigation required to predict the success of a reactive barrier system within a risk-based management strategy for 3 full-scale PRB industrial projects.

The potential benefit to a sustainable society is very large as there is a now a rapidly expanding interest in PRB technology in the UK where 2 new PRBs were completed in late 2003 to early 2004 and 2 are due for completion this year. There is anticipation that the technology will likely see 10 applications per year for the next 5 to 10 years. If each site provides a cost savings of approximately £1M (not unlike this project) or nearing £15M on one of the industrial projects, then a total saving to UK Plc would be between £55M and £825M.

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Extensive information on this project is available to download from the following website: http://www.prb-net.qub.ac.uk/eerg/dissemination/wpm/index.htm

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