

Assessment of the remediation options - Helpston waste disposal sites

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The Environment Agency and URS (formerly Dames & Moore) have been monitoring the migration of an extensive plume of contaminated groundwater in the Lincolnshire Limestone Aquifer, at Helpston, near Peterborough since the herbicide, mecoprop, was first detected at public water supply boreholes in 1988. The pollution originates from two former waste disposal sites (WDS), located 3km to the west of public water supply boreholes. Between 1999 and 2001, a series of studies were carried out to establish the best practicable technique for the remediation of both the contaminated land and groundwater.

In 1999, the source-pathway-receptor pollutant linkage had been established, but not properly characterised. In particular, the geometry and characteristics of the former WDS's and the structure of the complex geological in the immediate vicinity of the WDS's was not well understood. Nor was the fate and transport of the leachate, a complex mix of pesticides, metals and inorganic compounds, immediately surrounding the WDS's. Therefore, a series of intrusive investigations (including the construction and operation of a pilot treatment plant), waste characterisation studies, remedial feasibility studies and economic assessments were conducted to develop the most practicable and cost effective remedial strategy, for both contaminated land and groundwater.

This paper presents many aspects of these studies, concentrating on the following key issues, rather than the details of the remediation strategies:

- the setting of appropriate remedial objectives that are practicable, satisfy legislation and developing Agency guidance, when faced with large-scale areas of contaminated groundwater;
- the use of pilot systems and field trials to reduce uncertainties in the source-pathway-receptor pollutant linkage, leading to a greater degree of confidence in the remedial strategy; and
- economic evaluation of land and groundwater remediation.

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Natural attenuation of chiral mecoprop in the Lincolnshire Limestone

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Disposal of up to 40 tonnes of a racemic mixture of the phenoxyacid herbicide mecoprop into landfills in the UK Lincolnshire Limestone, has given rise to extensive groundwater pollution which has affected a public supply borehole 3 km away. In this study we focus on the fact that mecoprop is chiral, that is, it exists as two mirror images forms (enantiomers). Previous studies have shown that the enantiomers degrade at different rates, and therefore changes in the enantiomeric ratio could potentially constitute a useful indicator of natural attenuation.

Groundwater from 30 boreholes was comprehensively analysed and the concentrations of each mecoprop enantiomer and their stable carbon isotope ratios ($\delta^{13}\text{C}$) were

determined. The latter was included as additional evidence of biodegradation since microbial transformations often result in isotopic fractionation between reactants and products.

Change in enantiomeric ratio along a flow path from the landfill indicates that in the most polluted methanogenic and sulphate reducing zones, the mecoprop is still racemic, (i.e. it contains equal concentrations of the two enantiomers) even though the disposal of mecoprop ceased in 1991. This suggests that mecoprop does not degrade in these conditions. Further from the landfill, but still within the landfill plume, (*S*)-mecoprop dominates and could be explained by inversion of (*R*)- to (*S*)-mecoprop or faster degradation of (*R*)-mecoprop. With a change to aerobic conditions, an increase in the proportion (*R*)-mecoprop is explained by the faster degradation of the (*S*)-mecoprop in accordance with the literature. Associated changes in $\delta^{13}\text{C}$ were slight and inconclusive.

Laboratory microcosms using groundwater and crushed limestone left to acclimatise in the aquifer, showed that under aerobic conditions both enantiomers degraded with zero order kinetics with (*S*)-mecoprop degrading faster than (*R*)-mecoprop. Under anaerobic conditions in an identical microcosm (*S*)-mecoprop failed to degrade but (*R*)-mecoprop was transformed to 4-chloro-2-methyl phenol with Monod kinetics. The latter compound was stoichiometrically equivalent to the original (*R*)-mecoprop and only degraded once the (*R*)-mecoprop has disappeared. Addition of nitrate stimulated degradation in microcosms devoid of nitrate, or which were sulphate reducing. There was no evidence for enantiomeric inversion.

This study provides new evidence that mecoprop degrades under nitrate reducing conditions, and confirms that enantiomeric ratios can provide subtle evidence for *in situ* natural attenuation of mecoprop in the Lincolnshire Limestone.

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Responding to Pollution Events in the Context of Current Legislation: A Case Study of Bromate Contamination

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New Drinking Water Regulations due to be implemented in December 2003, include bromate as an additional parameter to be monitored. In May 2000, during preliminary sampling to identify the normal levels in water supply, bromate concentrations above the future standard were identified within a groundwater public supply source in the Three Valleys Water Company area. Low levels were also found in a second public supply source; in addition, some private water supplies were identified as being affected. A case study is presented identifying some of the key stages involved in responding to the pollution event, including short, medium and long-term activities.

The response activities and management of the impact of the contamination on groundwater sources and the aquifer at large are presented in the context of current legislation. In particular, the activities are related to the implementation of Part IIa of the Environmental Protection Act 1990, which came into force in England in April 2000. The legislation introduced a new regulatory regime for the identification and remediation of contaminated land.

The case study highlights the differing priorities and timeframes of stakeholder organisations, and the challenges presented by imprecise definition of roles and responsibilities. In addition, areas where lessons can be learnt are identified and questions posed regarding the management of similar pollution events.

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Validating processes of natural attenuation in a heterogeneous shallow aquifer

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This case study discusses the implementation of the Environment Agency's policy for Monitored Natural Attenuation (MNA) in a heterogeneous shallow aquifer. A poorly constrained source of contamination is producing a plume of dissolved phase benzene beneath a former gasworks. Monitoring shows that the extent of the plume is much less than predicted for the 30 year travel time, and that it fluctuates rapidly with time. Groundwater and contaminant transport models fail to predict this high variability. Inorganic groundwater chemistry and the loss of contaminant mass indicate that anaerobic biodegradation is occurring on site. This natural attenuation is considered to account for the limited extent of the plume and to protect the potential receptors. It is suggested that multiple lines of evidence can be used to validate MNA in cases where the development of a precise conceptual model by intensive data acquisition is not feasible in economic terms.

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1,000 f_{OC} measurements for UK geology and their value

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A major control on the attenuation of organic contaminants dissolved in groundwater is their sorption onto solid organic matter (OM) in the rock. Sorption modelling is currently based on the *amount* of solid organic carbon in the rock. However, there are very few available data on the fraction of organic carbon (f_{OC}) content in common UK geological materials. A significant new set of f_{OC} measurements for a range of aquifer and aquitard materials is presented and discussed in their geological context.

It is usually assumed that all organic matter will behave in the same way, disregarding the impact of the *type* of OM. Organic matter isolated from various geological samples was geochemically and micromorphologically characterised. These differences relate to the materials' K_{OC} , which varied over three orders of magnitude. Sorption was found to correlate with H/O content of the organic matter.

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Pesticide transport and degradation – A Danish perspective.

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Pesticides for weed control constitute the most frequent source of groundwater contamination in Denmark. The most frequently encountered compound in drinking water supply wells is BAM a metabolite of Dichlobenil, which has been extensively used at outdoors sports facilities, city parks, sidewalks, and private driveways in urban areas. The highest concentrations of pesticides (e.g. phenoxy acids, approaching 1 ppm) are encountered in upper groundwater near point sources such as cleaning areas for pesticide sprayers. Extensive research pertaining to the transport and degradation of pesticides in sandy aquifers and clayey till aquitards is being conducted in Denmark.

A 7 month long continuous injection of a mixture of 5 pesticides (bentazone, MCPP, dichlorprop, isoproturon, DNOC), a metabolite (BAM), and a tracer (bromide) was conducted in an aerobic aquifer. DNOC was significantly retarded, with spatial variation related to groundwater pH. After a lag-phase very fast degradation of MCPP and dichlorprop was observed. Slower degradation of DNOC was also observed.

Diffusion experiments with clayey till cores have verified significant retardation of pesticides by matrix diffusion. The retardation for some was lower than for bromide, due to the greater molecular size of the pesticides, and for others was greater than for bromide, due to sorption of the pesticides within the clayey till matrix.

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KEYNOTE ADDRESS

Source zone clean-up vs. plume management:

Is there a way to reach to an optimal decision ?

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The biggest challenges for many environmental scientists during the past 20 years have been the development of efficient tools for locating contaminants in soil and groundwater, and the design of cost-effective measures for the remediation of the subsurface environment. Various strategies were developed to either excavate, isolate or *in situ* flush (to decontaminate) the *contaminant source zones*, i.e. the locations where the contaminants have penetrated into the subsurface. However, thus far all source decontamination technologies available have proved to be only partially successful and very costly when applied to either larger sites or larger depths. Due to the diversity of conclusions published in the scientific literature during the past 2-3 years on this matter, the US EPA recently established an expert panel to analyse the pros and cons of so called “partial contaminant source clean-up” – that implicitly acknowledges the fact that there is no *in situ* technology available today that can clean-up a site to MCLs.

In practice, so far lacking any real alternatives, simple pump-and-treat concepts are commonly employed; i.e. the *contaminant plume* rather than the source is treated through downstream pumping wells. However, pump-and-treat itself might be very cost-inefficient if realistic operation periods of sometimes tens of years are considered. These findings are supported by site-statistics data, such as those published by the US NRC report (1994).

The important question remains: Is there a way to reach to an optimal decision about site remediation technologies? The answer is “maybe”!

In this paper the fundamental concepts as well as the present technical status of a decision support system, under development since 1997, will be presented. The system comprises a physical (advective) a chemical (reactive transport) and an economical (investment and operation cost) model system together with a general optimisation tool. The plume management options comprise pump-and-treat, reactive barriers, passive hydraulic barriers like slurry walls and (enhanced) natural attenuation. It includes cost-functions for the treatment of organic contaminants like VOCs, PAHs and BTEX. Uncertainty is introduced into the decision support system through a geostatistical description of subsurface heterogeneity and the possibility to consider ranges of parameters rather than fixed values. All that is evaluated together within a numerical stochastic approach (Monte Carlo) and leads to total costs (net present value) as a function of the anticipated overall system reliability. The system is being applied and tested at three so-called “megsites” in Bitterfeld (D), Rotterdam (NL) and Antwerp (B) to help identify optimal remediation options.

It should be noted that in the context of this paper source remediation is understood in terms of an *in situ* remediation. As this paper focuses on decision analysis based on risk assessment and cost-efficiency issues at large industrial sites, other remediation options like *in situ* containment or excavation are not considered here because these techniques are in general not applicable at large scale.

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In situ biodegradation of MTBE by indigenous microorganisms supported by diffusive oxygen release

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Methyl tertiary butyl ether (MTBE), added to fuel since the late 1980s to reduce smog-causing emissions, has rapidly become one of the most common groundwater contaminants in the US, UK and Europe. Due to its chemical characteristics and an apparent resistance to microbial degradation, MTBE tends to migrate at groundwater velocity and has, in many jurisdictions, impacted water supply wells and other sensitive resources.

We undertook a project at Vandenberg Air Force Base (VAFB) to study the controls on MTBE plume evolution, transport and fate. Early in that work, microcosm studies suggested that there were present at the site native microbes capable of aerobic MTBE biodegradation. TBA was generated during MTBE degradation but was subsequently degraded, suggesting that a consortium of organisms was active. Two *in situ* test facilities (panel and LFT) were constructed roughly 60 m downgradient of the source area to allow highly controlled evaluations of this indigenous population and to evaluate *in situ* treatment supported by a novel method of oxygen release by diffusion through polymeric tubing. Very shortly after

oxygen release began in both tests, significant decreases in MTBE concentrations were observed. TBA was observed downgradient of the panel on one occasion, supporting our hypothesis that the MTBE decrease was due to aerobic degradation. In both cases the reaction appears to be rapid: concentrations were reduced from ambient plume concentrations of 300-500 ug/L to ND in less than 1 m of travel distance. At the rate of groundwater flow, this corresponded to pseudo-first order degradation rates on the order of 5.7 day^{-1} .

A series of tests followed to 1) confirm that the decrease in MTBE was the result of degradation supported by oxygen release, 2) determine whether the microbial consortium could degrade higher MTBE concentrations, and 3) whether the consortium could degrade elevated MTBE concentrations in the presence of typical plume co-contaminant (toluene). When MTBE concentrations were increased or toluene introduced, a brief transient period occurred where MTBE migrated slightly further down the LTF, but treatment was subsequently reestablished at the rate previously observed. DGGE analysis revealed a shift in microbial population when toluene was added. These observations suggest that when MTBE concentrations were increased, the microbial community adapted by growing in numbers or increasing the rate of enzyme production, whereas when toluene was introduced, adaptation took the form of microbial diversification. These studies have demonstrated that *in situ* MTBE treatment is possible solely by enhancing dissolved oxygen concentrations, presumably within a permeable reactive biobarrier. However, our experience suggests that prior to full-scale PRB application at other sites, tests be conducted to 1) establish the presence and capabilities of native MTBE-degrading microorganisms, 2) measure the labile dissolved (and possibly solid) oxygen demand. The spatial variability of the plume and microbial capabilities may also need to be considered.

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Approaches to investigating the transport and fate of MTBE-amended petroleum hydrocarbons

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The management of contaminated land and groundwater is a challenging problem for many companies and local authorities. This is particularly the case in urban settings where there are frequently practical, technical and economical constraints that affect the scope of site characterisation and remediation programmes that can be implemented. The underlying problem is typically that of inaccessibility of the pollutants and heterogeneity in site conditions. This makes the assessment of pollutant distribution and fate frequently very difficult and expensive.

Of recent concern is the environmental behaviour of oxygenate compounds, in particular methyl tert-butyl ether (MTBE), which are added to petroleum fuels to improve combustion and reduce atmospheric emissions. The widespread usage of MTBE in the UK, since the mid-eighties, has resulted in the contamination of major aquifers, including the Chalk aquifer of southern England. Restoration of MTBE and BTEX (benzene, toluene, ethyl benzene and xylenes) contaminated groundwater to acceptable limits is technically difficult and costly; therefore, natural attenuation (NA) is being evaluated as a potential remediation option.

We present a methodology which integrates techniques to determine aquifer geological, hydrogeological and hydrochemical characteristics, which include the analysis of rock core, downhole geophysical fracture logging, vertical hydraulic profiling and multilevel sampling of

vertical solute profiles to understand controls on the distribution of contaminants and biodegradation processes in the aquifer. The study shows that contaminant fate and transport is controlled significantly by the fracture network, contaminant properties and biodegradation. The adoption of the methodology incurs higher “up-front” costs in site investigation, but provides a higher quality dataset, improved confidence in the interpretation of contaminant fate, reduced uncertainty in risk assessment and more cost-effective remediation. The approach is likely to be appropriate and of value in the investigation of contaminated sites on other aquifers.

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An evaluation of leaching test methods for assessing the impact of contaminated land on rising groundwater in an area of urban regeneration

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Due to the closure of traditional industries in many UK conurbations, groundwater abstraction has declined and, in some areas this is leading to the saturation of industrially contaminated land and wastes. This provides the potential for the mobilisation of contaminants to the detriment of aquifers and surface waters. Research has been undertaken to investigate the potential for such groundwater contamination in the City of Wolverhampton that partly overlies an important Permo-Triassic sandstone aquifer.

The research has investigated a range of fills and waste materials, typical of the area, including foundry sands, metal smelting slags, colliery spoil and domestic refuse. These have been subjected to detailed chemical and mineralogical characterisation and a range of leaching tests.

An in depth study was undertaken comparing the influence of the leaching test method and choice of leachant on the results and subsequent interpretation. The leachable concentrations of heavy metals, metalloids and anions were determined using a range of batch, column and multi-stage leaching methods. A number of tests explored the effects of varying leachant composition to simulate different groundwater chemistries. These included uncontaminated groundwater, rainwater, acid minewater and landfill leachate.

Although the majority of the samples investigated are highly contaminated with various heavy metals, these were not available under the various environmental scenarios investigated and therefore could be classed as chemically inert. The data indicate that column tests typically indicated higher leaching of contaminants than the standard batch test, while the multi-stage test is a good compromise between the limitations of the standard batch test and the complexity of column testing. The choice of leachant was found to have a moderate influence on the leaching response. The general interpretation is that the contaminants have either historically been present in a non-available form, or if ever present in an available form have been leached by rainwater over time. Therefore, even the most extreme natural groundwater envisaged will not significantly leach further contaminants.

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Perched groundwater in mine spoils: hydrogeology and remedial options

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Many of the larger mine spoil heaps in northern England host perched aquifer systems. The groundwater in such systems is often of very poor quality due to pyrite oxidation and other geochemical processes. Where such groundwaters discharge to surface water courses (either as diffuse or point emissions) they cause serious damage to aquatic ecosystems. Studies of three spoil heaps in NE England (at Shilbottle, Quaking Houses and Bowden Close) are revealing some of the internal hydrogeological functioning of these idiosyncratic man-made aquifers, as well as providing the basis for innovative passive treatment systems (PRBs, compost wetlands and a type of subsurface-flow bioreactor termed a RAPS), based on hydrogeological and geochemical principles, which seek to achieved sustained, long-term remediation of this form of pollution.

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Contaminated land meets groundwater meets surface water: Birmingham – River Tame case study

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Contaminated land may impact underlying groundwaters that may in turn impact surface waters. The European Water Framework Directive requires the integrated management of the above and provides the underlying rationale to a variety of research studies conducted by The University of Birmingham over the past 4 years on the Birmingham aquifer – River Tame system. Of particular interest is the impact of contaminated land in Birmingham on the 8-km long reach of the River Tame that crosses the effluent, unconfined Birmingham Triassic sandstone aquifer. We have obtained quality data-sets from contaminated soils, deep abstraction boreholes, shallow monitoring wells, river-bed piezometer data and surface water. The river-bed piezometer data set (approaching 100 piezometers have been installed) collected as part of an Agency-supported PhD studentship (Ellis, P.A.) is the main focus and briefly presented.

The river-bed piezometers have successfully indicated the nature (quantity and quality) of baseflow to the river and chlorinated solvents, metals, F⁻, Cl⁻ impacts are shown for example. Significantly more piezometer installations (and supporting data), however, would be required to discern the nuances of specific contaminant plume discharges to the river and also estimate a more reliable contaminant loading to the river from contaminated land - contaminated groundwater sources. Contaminated baseflow plumes discharging to the river are, not unexpectedly, spatially discrete with marked contrasts in baseflow quality emerging

from opposite banks at a given river position. Natural attenuation of organic contaminants has not been particularly observed to date in the hyporheic zone, nevertheless there is evidence of biodegradation controls occurring during prior aquifer transport.

To date, quality impacts of Birmingham groundwater on the River Tame are perceived fairly low, even positive in relation to some contaminants on this poor-quality urban river. It is clear from this study that much underpinning science is still required to permit a process-based implementation of the Water Framework Directive in relation to both urban and rural contamination scenarios.

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The Water Framework Directive – Developments affecting groundwater and contaminated land

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The EC Water Framework Directive will establish a new integrated approach to the protection, improvement and sustainable use of surface water and groundwater. The Directive came into force in December 2000 and will be implemented over the coming decade with UK legislation due by the end of 2003. River Basin Management Planning is the delivery mechanism for the WFD's environmental objectives, consisting of characterisation, risk assessment, monitoring, setting of local objectives, and design and implementation of measures to achieve these objectives, all on a six year planning cycle. Though the first plan runs from 2009-2015, a substantial amount of preparatory work is needed and all water bodies must be delineated and initially characterised by December 2004 (a water body being the management and compliance assessment unit under the WFD). Groundwater quality is an outstanding issue and under Article 17 of the WFD the EU Commission must present proposals to the European Parliament for a new Groundwater Directive by December 2002. This will eventually replace the existing Groundwater Directive.

The Environment Agency has just launched a consultation on Annexes II and V of the WFD, which detail the technical heart of the River Basin planning system. The presentation will describe these technical aspects, concentrating on groundwater, in the context of overall WFD objectives, together with the potential implications of the Groundwater Daughter Directive. Contaminated land, as a pressure on water bodies, will potentially fall within the scope of any measures required to meet WFD objectives. The potential changes to current approaches to groundwater protection and contaminated land that may arise from the new legislation will be discussed.

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