C L : A I R E

SB 1

(August 2005)

site bulletin

CL:AIRE site bulletins provide a source of background information on sites which have been used within the scope of CL:AIRE technology demonstration and research projects. This bulletin describes a monitored natural attenuation site.

Management of a Petroleum Plume by Monitored Natural Attenuation

1. INTRODUCTION

The purpose of this bulletin is to describe the practical aspects of managing a monitored natural attenuation (MNA) scheme at a site on the chalk aquifer and particularly focuses on the roles of the various stakeholders. A petrol leakage from an underground storage tank occurred at the site which resulted in groundwater contamination of the underlying Chalk aquifer with the need to manage the groundwater contamination. MNA has formed an integral part of the overall management strategy for contamination at the site.

This site was also the subject of an EPSRC research project undertaken by the University of Sheffield into the degradation of hydrocarbons in groundwater and was the topic of CL:AIRE Case Study Bulletin 1.

2. BACKGROUND

The petrol station site is located in an urban area. An accidental loss of approximately 55,000 litres of unleaded petrol from an underground tank was identified by the operator in February 1999. This loss was immediately reported to the Environment Agency and the following measures were implemented:

- Repair (lining) of the underground tank;
- Construction of investigation boreholes, within and up and down hydraulic gradient of the petrol station forecourt, to determine the extent and degree of any groundwater contamination;
- Product recovery. The rates of recovery were very low such that it was not effective to continue with this measure; and
- Implementation of soil vapour extraction scheme. This proved successful and it is estimated that some 50 % of the lost fuel was recovered over a two year period.

The petrol station was closed in April 2002 and decommissioned in October 2002. The site is underlain by 6 m to 8 m of drift deposits which overly the Chalk. The water table is some 20 m below ground level and groundwater flow is to the southeast. The station also falls within the groundwater protection zone to a public water supply source operated by Veolia Water UK. The water supply source is located some 4 km to the southeast of the site.

When the underground tanks were removed as part of site decommissioning, the tanks were found to be underlain by silty clay with sand and gravel lenses. The sand and gravels provided a pathway for movement of the lost petrol down to the underlying Chalk.

The first phase of investigations identified that groundwater below the site was contaminated mainly by benzene, toluene, ethylbenzene, xylene (the BTEX compounds) and the fuel oxygenates methyl tertiary-butyl-ether (MTBE) and tertiary-amyl methyl ether (TAME). BTEX compounds were identified in boreholes up to 50 m from the site and MTBE and TAME in boreholes 100 m to the south of the petrol station. Some Light Non Aqueous Phase Liquid (LNAPL) was found in the monitoring boreholes drilled within the petrol station site (typical NAPL thicknesses of less than 1 cm); trials to recover this NAPL proved that only limited recovery was possible. A simplified conceptual model of the site is shown in Figure 2.

3. MONITORED NATURAL ATTENUATION

Monitored natural attenuation (MNA) as a remediation strategy relies on natural attenuation processes in the aquifer being effective in preventing migration of a contamination plume. These processes can be extremely effective in reducing contaminant concentrations and therefore prevent the need to implement other measures such as pump and treat.

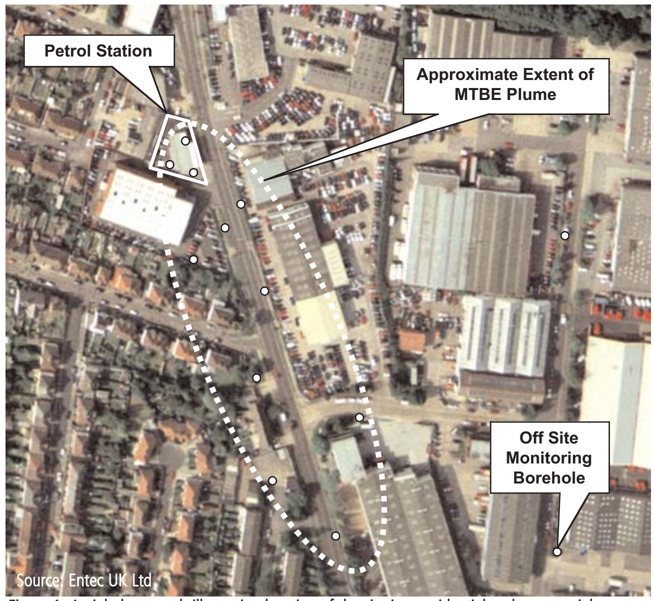


Figure 1: Aerial photograph illustrating location of the site in a residential and commercial area, and showing the location of monitoring boreholes and the approximate extent of the MTBE plume.

The stages in development of a plume following a contaminant release will be initial expansion of the plume, followed by steady state and finally a shrinking plume. The development of steady state represents balance between contaminant flux and attenuation processes. On identification of groundwater contamination the first stage in its assessment is determining whether the plume is migrating and whether this represents a risk to downgradient receptors. If so then mitigation measures need to be implemented.

The Environment Agency has published guidance on the assessment of MNA of contaminants in groundwater (Environment Agency, 2000). This guidance sets out the criteria for determination of whether MNA is an appropriate remedial strategy at a site. The assessment should be undertaken as a series of stages as illustrated by Figure 3, including consultation and liaison with relevant regulators and affected parties. Fundamental to the approach is identifying lines of evidence that demonstrate that natural attenuation processes will be effective in reducing contaminant concentrations and in preventing migration of the plume such that there would not be a risk to downgradient receptors.

4. ASSESSMENT OF MNA

In order to assess whether natural attenuation was likely to be effective at the site the following tasks were undertaken:

- Literature review to establish whether compounds present in the fuel would be expected to degrade. This review identified that there was strong evidence that BTEX compounds can degrade, but that there were conflicting data on the conditions under which MTBE and TAME would degrade. In addition the review identified there were limited published data on degradation in the Chalk aquifer;
- Plotting the distribution of hydrocarbons both spatially and with time to determine whether there was evidence that concentrations were decreasing, steady or increasing. In particular for a fissured Chalk aquifer, rates of contaminant migration might be expected to be high, of the order of metres per day, the

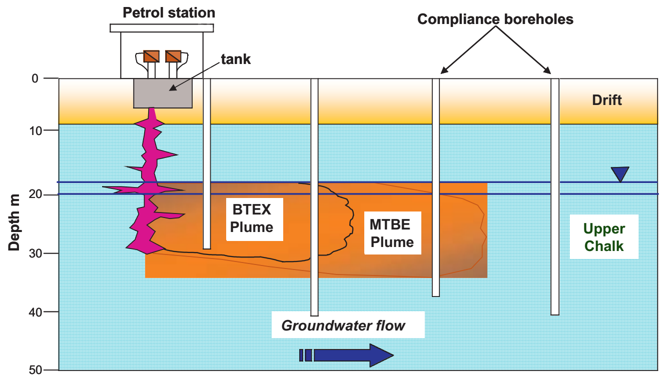


Figure 2: Simplified conceptual section of the site

Source: Entec UK Ltd

observation that 2 years after the original spill the hydrocarbon plume only extended some 100 m from the petrol station indicated that attenuation in the aquifer was high. This attenuation was considered to be a function of diffusion of hydrocarbons in fissure water into the chalk pore water and degradation. Fissure to pore water exchange can result in a significant reduction in the rate of contaminant transport due to the much larger volume of pore water;

- Evaluating whether there were indirect indicators of degradation processes such as depletion of electron acceptors (dissolved oxygen, nitrate and sulphate) and an increase in electron donors (iron and manganese) in groundwater. Monitoring data show a pronounced depletion in dissolved oxygen, nitrate and sulphate concentrations in the plume centre. Electron balance calculations also indicate that principal electron acceptors are nitrate and dissolved oxygen and that there was a sufficient supply of electron acceptors to support degradation;
- Numerical modelling to establish whether the observed distribution of BTEX and MTBE could be modelled and to then use the numerical model to predict hydrocarbon concentrations in order to determine whether there is a risk to downgradient receptors including the public water supply source. This exercise indicated that the observed distribution and variation with time of BTEX compounds was consistent with degradation and diffusion exchange between fissure water and pore water. Model predictions indicated that further migration of the BTEX plume was unlikely. For MTBE, modelling indicated that its distribution could largely be explained by fissure/pore water migration and that the rate of degradation was slow such that some expansion of the plume might be expected before steady conditions were reached.

The conclusion from this work was that there was strong evidence that MNA was a viable remedial solution for BTEX, but that there was uncertainty as to whether degradation of MTBE was occurring and whether this was at a rate sufficient to prevent migration of the plume. Therefore further information was required to provide a better understanding on MTBE degradation.

For this reason, in implementing MNA at this site, the following additional work was deemed necessary:

- Construction of additional monitoring boreholes; the most downgradient borehole is located some 400 m from the site;
- Routine monitoring; a monitoring network was put in place (including multi-level boreholes) with monitoring undertaken monthly;
- Derivation of trigger levels to provide a basis for assessing whether MNA was behaving according to expectations and to provide a trigger for further work or for mitigation measures to be implemented;
- Routine reporting to the Environment Agency including annual update of the risk assessment and supporting conceptual model;
- Research by the University of Sheffield (Wealthall *et al.*, 2002; Spence *et al.*, 2005) into the factors controlling attenuation of BTEX and MTBE including laboratory microcosms studies to determine the controls and rates of degradation.

Associated with this work was a review of alternative remedial options such as pump and treat and enhanced bioremediation (through release of dissolved oxygen or chemical oxidants). The major difficulty in implementing these options at this location is land ownership and access such that the cost of implementing alternative options is high. Therefore MNA, if confirmed, represents the most viable remedial option at this site.

5. STAKEHOLDERS

Essential to the management of the site has been the involvement of different stakeholders.

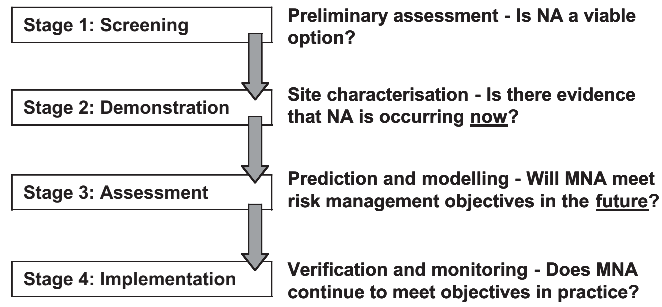


Figure 3: Stages in the assessment of natural attenuation

Source: Entec UK Ltd

The main stakeholders are the site operator (Total UK Ltd), the Environment Agency, Veolia Water UK, the University of Sheffield and Entec UK Ltd acting on behalf of Total UK. Additional parties include adjacent property owners, local residents, and the Highways Authority. The standpoint of these stakeholders is described below:

Total UK Ltd operated the petrol station and has the liability for the groundwater pollution resulting from the spill. Their main criteria in their acceptance that MNA was an appropriate strategy at this site were that the solution represented the best option in terms of practicality, environmental benefit, cost effectiveness, time to achieve closure and this measure is a more effective solution than other remedial measures. Total UK also adopted a pro-active approach to this site in working with the Environment Agency, supporting the research project by the University of Sheffield and supporting implementation of the monitoring scheme through negotiation with third parties.

The Environment Agency's main requirement for the operation of the site as an MNA site is that there should be no significant deterioration of groundwater quality downgradient of the petrol station and in particular that the public water supply source is not placed at risk. The Agency also has a requirement to promote research and has supported the EPSRC research project undertaken at the site. Therefore the project has involved:

- Providing evidence to the Environment Agency that attenuation is occurring at a sufficient rate to protect water resources;
- Derivation of trigger levels and an associated action plan that would be implemented in the event of the trigger levels being exceeded;
- Routine monitoring to verify the effectiveness of NA;
- Reporting the results of the research project;
- On-going liaison with all stakeholders to facilitate progress.

The Agency has also provided additional support in liaison with land owners in obtaining permission to drill monitoring boreholes.

Veolia Water UK operates the public water supply located about 4 km to the southeast of the petrol station. The petrol station site is located within the source protection zone to this site. In adopting MNA as the remediation strategy at this site it has been necessary through monitoring and on going risk assessment to demonstrate that this source is not at risk.

The site has provided an opportunity to undertake a detailed research project on the fate and transport of hydrocarbons in the Chalk. This project was sponsored by EPSRC and was led by the University of Sheffield. Details of this project are described in Spence *et al.*, (2005). The research focussed on the attenuation of MTBE and BTEX compounds in the Chalk and in particular on understanding the controls and rate of degradation of these compounds. One of the key benefits of selecting this site for the research was that it provided the opportunities to investigate in detail a plume under natural conditions. Outputs of this project relevant to the improved knowledge of the management of the site were the improved characterisation of the Chalk aquifer, improved understanding of plume behaviour and attenuation processes and, in particular, evidence of the degradation of BTEX and MTBE.

The primary role of the consultant, Entec, was to manage the site in terms of:

- Communication and working with key stakeholders;
- Undertaking site investigations, borehole drilling and routine monitoring;
- Assessment of the effectiveness of MNA as a remedial strategy and whether alternative measures need to be implemented;
- Advising Total UK on technical, economic and regulatory aspects of management options.

6. BOREHOLE CONSTRUCTION AND ACCESS

Essential to the assessment and monitoring of a MNA site is the ability to construct monitoring boreholes within and around the plume to understand its behaviour and to demonstrate that NA processes are effective in preventing migration of the plume. Construction of off-site boreholes can normally only be achieved by negotiation and with the co-operation of other site owners, and the time to obtain agreement can be lengthy. In the event of problems in gaining agreement, the Environment Agency can implement powers under the Water Resources Act, 1991 (Section 161A) to require a borehole to be located on private land when third party (the land owner) agreement cannot be obtained. This still allows the owner to be granted compensation, subject to arbitration.

The site presented a potential difficulty for the construction of monitoring boreholes due to its location in a residential and industrial area as illustrated in Figure 1. This was overcome by negotiation with property owners and locating boreholes along the verges of roads, within parking areas for industrial sites and garage parking for private properties. Obtaining permission for these boreholes has required: obtaining a street works permit from the Highways Authority to construct monitoring boreholes, liaison with utilities on the location of services, agreeing footpath closure and traffic management with the Highways Authority and local police. For boreholes drilled on private land the process has involved explaining the reason for and the nature of the work to residents, providing a method statement for the work (covering access, hours of working, reinstatement), legal agreement between Total UK and the site owner, liaison with the site owner during the work, and completing the work within an agreed time period. This required input from Total UK in meeting and talking to the site owner, co-operation by the site owner, the support of the Environment Agency in addressing additional questions of the site owner and the consultant in managing the process and in developing a working understanding of the requirements of the different parties. The time between identifying an off-site borehole location and completing its construction typically varied from 3 to 6 months depending on the complexity of discussions over access.

The above illustrates that implementation of a comprehensive monitoring scheme in an urban setting is not straightforward, it requires patience and understanding from all parties.

The boreholes have been constructed in a number of phases, as it became necessary to improve our understanding of the plume and to accommodate difficulties in obtaining access. Each phase of drilling has been accompanied by leafleting local residents explaining the nature of the work, placing posters around the working area and liaising with property owners.

The works associated with each borehole have involved drilling, coring to provide samples for laboratory testing, geophysical logging, packer testing to determine the vertical variation in aquifer properties and groundwater quality and installation of multiple or single sample points. This work was considered essential to understanding the vertical as well as lateral behaviour of the hydrocarbon plume.

For one of the borehole locations a public meeting was organised by Total UK in which the reason for drilling and monitoring was explained, the disruption caused by drilling described, and questions by local residents addressed. This resulted in a working arrangement being developed which minimised disturbance to local residents and arrangement with residents for the temporary relocation of vehicles.

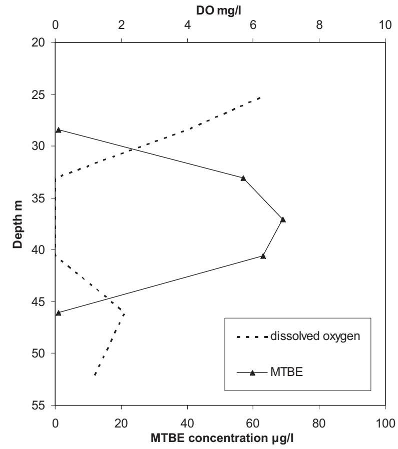
The approach of talking and working with site owners and residents, involving them through understanding their concerns and explaining what the project is trying to achieve, has been proven to be effective and resulted in co-operation from both parties.

7. MONITORING AND EVALUATION OF RESULTS

The monitoring boreholes constructed at the site have comprised single open boreholes and multi-levels boreholes. A separate CL:AIRE publication (Technical Bulletin 2) has been produced describing the multi-level boreholes. The main purpose of the multi-level boreholes was to define the vertical distribution of the hydrocarbon plume as packer testing and pore water profiling identified that there was significant variation in groundwater chemistry. This vertical information has proven to be important in understanding the behaviour of the plume. An example of the vertical distribution of MTBE and dissolved oxygen in a monitoring borehole is shown in Figure 4.

Twenty-two boreholes have been constructed within and outside of the petrol station forecourt. The locations of the boreholes are shown in Figure 1.

Sampling included measurement of groundwater level, purging each borehole prior



Source: Entec UK Ltd

Figure 4: Depth profile to illustrate relationship between MTBE and dissolved oxygen concentrations

to obtaining water samples for laboratory analysis and field measurement of selected parameters (such as dissolved oxygen). Routine laboratory analysis include BTEX, MTBE and TAME. Samples were also obtained for analysis of electron acceptors (nitrate, sulphate) and electron donors (iron, manganese) to establish whether the geochemical environment is changing (i.e. evidence of a decrease in dissolved oxygen and nitrate concentrations which could indicate the potential for hydrocarbons concentrations to increase due to exhaustion of electron acceptors which support microbiological degradation).

The number of boreholes sampled each month varied. Every 3 to 4 months all of the boreholes were sampled to allow the vertical and lateral extent of the plume to be mapped. Between these full monitoring rounds selected boreholes were sampled to provide information on the variation in hydrocarbon concentrations with time. Monthly monitoring was necessary due to the observed seasonal variation in groundwater levels which results in variations in the direction of groundwater flow and contaminant flux with time.

Each sampling exercise could take 2 to 5 days depending on the number of boreholes sampled. With the number of samples ranging from 20 to 60, it is evident that the implementation of monitoring at this site was not a cheap option. The cost of each multi-level borehole being about £15K and the annual cost of monitoring in the order of £45K per year. However the monitoring effort at this site is greater than would normally be undertaken due to the need to provide additional data to support the research study and due to the sensitivity of the site over a major aquifer.

The monitoring results are entered into a database and plots produced of the spatial and temporal variation in hydrocarbon concentrations. The results are compared with trigger levels and, following assessment and interpretation, presented to the Environment Agency. Examples of the time series plot are presented in Figure 5.

For each monitoring exercise, an 'Operational Protocol' was followed which required adherence to a health and safety plan, liaison with site owners, and procedures to collect and dispose appropriately of the purged water. The operation of sample pumps close to residential properties can cause nuisance and this has been managed by liaising with residents.

8. TRIGGER LEVELS

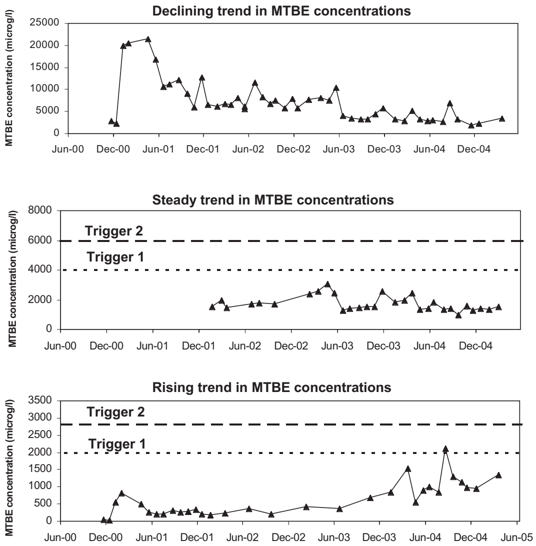
Part of demonstrating that MNA is behaving according to expectations is the comparison of the monitoring data with trigger levels. If concentrations remain below the trigger levels then it can be concluded that the plume is behaving according to expectations and NA is proving to be effective in preventing migration of the plume. If the trigger levels are exceeded then this indicates that the plume is expanding and that further investigations and mitigations need to be implemented.

Trigger levels were derived using model predictions on the rate of contaminant movement and analysis of the initial monitoring data taking into account that the plume had already migrated off site. In the longer term, trigger levels will be derived to demonstrate that the plume is shrinking and, therefore, monitoring would no longer be required.

Two trigger levels were set; exceedence of which would instigate the following actions:

Trigger Level 1

- An increase in frequency of monitoring to fortnightly (to confirm the trend);



Source: Entec UK Ltd

Figure 5: Plots illustrating the variation in MTBE concentrations with time to show the range of trends observed in monitoring boreholes. Trigger levels for two of the boreholes are also shown.

- A review of the risk assessment;
- A report to the Environment Agency to be provided within 1 month of confirmed exceedence on the proposed action plan.

Trigger Level 2

Depending on the observed behaviour of the plume, implementation of an action/contingency plan which comprises:

- Drilling of additional monitoring boreholes;
- Further modelling to re-assess plume behaviour;
- Further investigations into attenuation;
- Implementation of additional mitigation measures such as pumping to prevent migration of the plume and/or release of oxygen or chemical oxidants to promote *in situ* degradation. In introducing such measures the principal limitation at the site was access in terms of drilling boreholes to house pumping or oxygen release equipment.

An example of a plot showing the variation in hydrocarbon concentrations in comparison to trigger levels is shown on Figure 5.

9. MAIN OBSERVATIONS FROM ROUTINE MONITORING

Routine groundwater monitoring has been undertaken since 1999. This monitoring has shown that the hydrocarbon plume is orientated along a northwest to southeast axis and parallel to groundwater flow. The monitoring data also indicates that the centre of the plume can oscillate slightly in a west to east direction due to seasonal changes in groundwater flow. This seasonal oscillation can result in a variation in the trends (i.e. a mixture of rising and falling trends) observed in some boreholes, depending on their location in relation to the plume (Figure 5).

The spatial extent of the different hydrocarbons varies in relation to their geochemical properties. MTBE and TAME show the greatest longitudinal extent and have been detected in boreholes some 200 m downgradient of the petrol station. These hydrocarbons are characterised by the highest solubility and are less likely to degrade compared to BTEX compounds. The BTEX compounds have been detected occasionally in boreholes located some 100 m downgradient of the petrol station, however, monitoring has demonstrated that the BTEX plume is shrinking as illustrated by Figure 6. Of the BTEX compounds benzene shows the greatest lateral extent.

The long-term monitoring data have shown that the concentrations and lateral extent of BTEX compounds in groundwater has decreased with time. For MTBE the picture is more complicated. In boreholes near to the source concentrations have been observed to decrease; in the plume centre concentrations have remained steady; whereas at the front of the plume increases in concentrations have been observed in some boreholes. This trend is complicated by seasonal variation in the orientation of the plume.

10. MAIN RESEARCH FINDINGS

The research project has provided strong evidence that degradation of BTEX compounds is occurring and explains the observed behaviour of the plume. These conclusions are based on evidence from stable isotope analysis, microcosms studies

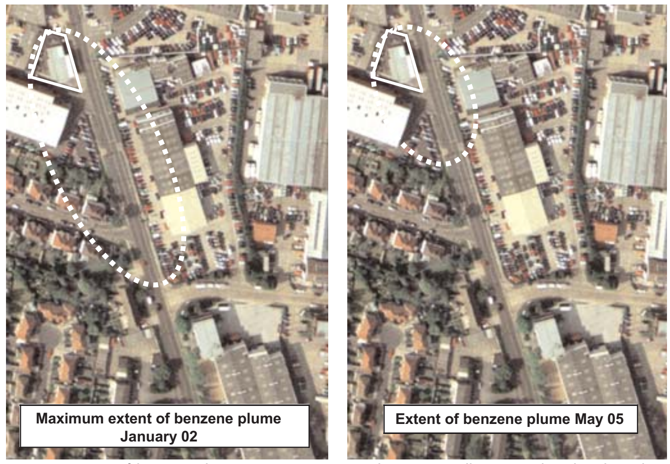


Figure 6: Extent of benzene plume in January 2002 and May 2005 illustrating that the plume has shrunk with time.

Source: Entec UK Ltd

and contaminant modelling (Spence *et al*., 2005). The research has also identified the potential for the degradation of MTBE and TAME. Laboratory studies indicate that this degradation can be relatively rapid with half lives of the order of tens of days. The research has provided information on factors controlling whether degradation occurs or not, a key control being the presence or absence of dissolved oxygen. Field data show that the presence of MTBE is always associated with the absence of dissolved oxygen, as illustrated by Figure 4. The conceptual model for the site shows that in the centre of the plume degradation of other hydrocarbons (e.g. BTEX compounds) occurs preferentially, resulting in the depletion of dissolved oxygen and the inhibition of MTBE degradation. At the outside edge of the plume where other hydrocarbons have been removed and where dissolved oxygen is present, then MTBE and TAME degradation can occur.

This understanding has resulted in a change in the monitoring programme with greater emphasise being placed on boreholes located at the margins of the plume and measurement of dissolved oxygen concentrations in groundwater.

11. EXIT PLAN

The final goal in operating an MNA strategy at a site is to demonstrate that the site no longer represents a risk to water resources and that monitoring can cease. This point is reached when monitoring data shows falling trends in contaminant concentrations and that confidence can be attached to the conclusion that the contaminant concentrations no longer represent a risk and concentrations can be expected to return to background levels.

12. SUMMARY

The main lessons that have been learnt from this project are that on-going development of the conceptual model of the behaviour of the plume is essential to verifying that MNA is a viable option. The establishment of a monitoring network has been critical to understanding the behaviour of the plume. Given the initial uncertainty into the behaviour of MTBE and the importance of the Chalk aquifer then it was necessary to construct boreholes inside and outside of the plume and to undertake monthly monitoring to provide confidence that the plume was not expanding at a rate that would pose a risk to downgradient receptors. Management of an MNA site can involve a number of stakeholders and, therefore, a key to the successful operation of a scheme is regular liaison to ensure that each party is confident that their objectives are being dealt with.

ACKNOWLEDGEMENTS

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