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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 research bulletin provides guidance on comparative assessment of approaches to predicting the fate and transport of dissolved-phase hydrocarbons in Chalk aquifers.

Modelling approaches for assessing risks associated with petroleum hydrocarbon spills in the UK Chalk aquifer

1. INTRODUCTION

This bulletin summarises the findings of the project "Comparative assessment of approaches to predicting the fate and transport of dissolved-phase hydrocarbons in Chalk aquifers", sponsored under the DTI LINK Bioremediation Programme and endorsed by CL:AIRE as a Research Project. The full findings of the project are summarised in the project final summary report (Wright et al, 2007).

The modelling studies evaluated a suite of analytical and numerical fate and transport models for their application in simulating dissolved-phase contaminant migration in groundwater at three petroleum filling station sites. The performance of each model in predicting the observed spatial and temporal distribution of dissolved contaminants in the saturated zone was compared. Combining lessons learnt during the calibration process and the comparative review of the model performance at each site has allowed recommendations to be made for quantitative risk assessment in the Chalk aquifer. The principal lesson learnt from the project was that groundwater velocity is the most critical parameter, and if it can be adequately constrained then the results of the modelling predictions will be significantly improved.

Three sites were identified at which a release of unleaded petrol into the Chalk aquifer had occurred, resulting in the development of a mixed petroleum hydrocarbon and ether oxygenate (Methyl Tertiary Butyl Ether (MTBE) or Tertiary Amyl Methyl Ether (TAME)) plume in groundwater flowing beneath and down-gradient of the sites. Site investigations had been undertaken at each site, using different design strategies and investigative techniques. The investigations at each site included groundwater elevations and contaminant concentrations. One of the sites (referred to as Site 1) was operated as a research site by the University of Sheffield (UoS) with Entec UK Ltd and therefore more detailed investigation data were collected than is commonly available through a routine commercial investigation (Thornton et al, 2006; Wealthall et al, 2002).

The site data were used to develop hydrogeological conceptual models for each site which formed the basis for the modelling. The conceptual model for Site 3 is presented for illustration in Figure 1.

The key project objectives were to:

- assess the characteristics and performance of simple and more complex mathematical models for each Chalk site;
- identify which modelling methods are best suited to the variable conditions and conceptual models present at different contaminated Chalk sites; and
- provide guidance to quantitative risk assessment practitioners, based on the conclusions of the study.

The full details of the project and the results can be found on the website: www.chalkfti.co.uk and in the final project report (Wright et al, 2007).

2. THE UK CHALK AQUIFER

The project focussed on the Chalk aquifer as it provides 55% of the groundwater supply in the UK (Lloyd, 1993) and is also highly vulnerable to contaminant spills due to its extensive geographical distribution and characteristic double porosity (also known as dual porosity) structure.

The aquifer comprises blocks of very fine matrix material which form the primary porosity and fractures which form the secondary porosity and represent typically only 1% of the bulk rock volume. Groundwater flow is primarily via the fractures. The large volume of relatively immobile water stored within the matrix can have a different chemistry to the neighbouring fracture water at contaminant spill sites. Diffusion of dissolved contaminants between the fractures and matrix has a strong control over the solute concentrations within the fracture waters over long periods of time.

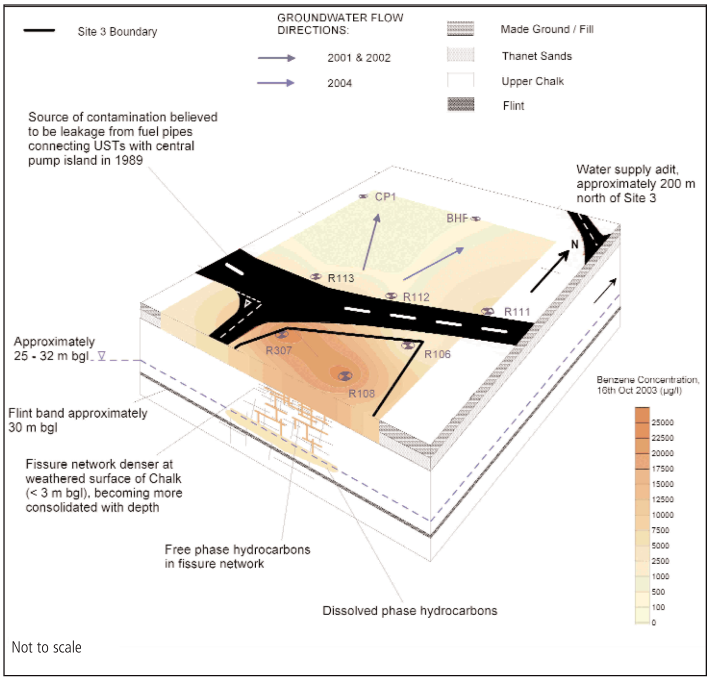

Fig. 1: Hydrogeological Conceptual Site Model for Site 3

3. MODEL SELECTION

Five public-domain contaminant fate and transport models were used to simulate contaminant distribution and migration at each site. Selection of the five models was based on a screening evaluation of more than 50 models that took into account the commercial availability and cost within the UK, the model capabilities in terms of transport and attenuation processes, data requirements and therefore the implied site investigation costs.

The final model selection aimed to assess the value of including different components and processes within the contaminant transport simulations, including steady-state and transient source terms, double-porosity diffusion processes, detailed biodegradation modelling (i.e. simulation using Monod kinetics, as opposed to the commonly applied first-order approximation), as well as 2-D and 3-D models and transient groundwater flow.

The models selected were simple 1-D fate and transport models (Environment Agency Remedial Targets Worksheet, P20 and a double porosity model, DP1D). At Site 1 more complex numerical models (MODFLOW/MT3DMS, PHREEQC and TRAFRAP-WT) were also applied as more data were available than for the other sites. The functionality and availability of each of the models used is presented in Table 1.

4. MODELLING APRROACH

Following calibration, each model was validated using a series of model predictions on monitoring wells at selected times and locations using data not included within the calibration. Model performance was principally assessed using qualitative criteria, consisting of visual inspection of the modelled contaminant concentrations against the observed data used for the validation boreholes.

The assessment criteria comprised:

- time of contaminant breakthrough in monitoring wells;

Table 1: Model Code Functionalities

	Dispersion	Degradation	Double Porosity Implementation	Sorption	Dimensionality	Reference
Environment Agency Remedial Targets Worksheet (v2.2a) *	3-D	1st order	None (single porosity only)	Yes	1-D	Remedial Targets Worksheet v2.2a produced for use with Marsland & Carey (1999)
DP1D	1-D	1st order	Fickian	Yes	1-D	Barker (2007)
TRAFRAP-WT	3-D	1st order	Fickian	Yes	2-D	Huyakorn et al. (1987)
MODFLOW / MT3DMS	3-D	1st order / Monod Kinetics	Quasi-Steady-State Approximation in MT3DMS**	Yes	3-D	MODFLOW: McDonald & Harbaugh (1988) MT3DMS: Zheng et al. (1999)
PHREEQC	1-D	1st order / Monod Kinetics	Quasi-Steady-State Approximation**	Yes	1-D	Parkhurst & Appelo (1999)

* v2.2.a was current at the time of the project but has now been superseded by the Remedial Targets Methodology 2006, however the results of project remain valid.
** the double porosity is characterised as two fully mixed volumes, solute transport between the volumes is described by a mass transfer coefficient.

- long-term average contaminant concentrations; and
- temporal evolution of contaminant concentrations in monitoring wells.

5. MODEL CALIBRATION

Overall, the models provided equally good calibrations to each data set, using reasonable input parameters. Because of this it was not possible to identify the most appropriate model on the principle that it provided the best calibration. Both DP1D and P20 were successful in simulating the mean contaminant concentrations; however the DP1D model could represent changing solute concentrations over time better than the P20 model. This can be seen in Figure 2 and is the result of the constant input concentration defined in P20 (Figure 2, bottom), compared to a more flexible source term in DP1D (Figure 2, top). DP1D was made to emulate P20 with the added functionality of variable input concentration.

The most notable outcome of this procedure was that calibration of different contaminants at the same location resulted in different predicted flow characteristics. This was apparent by comparing the calibrated flow velocities and is likely to result from the non-uniqueness of the models. This does not allow the parameter ranges to be sufficiently well refined, resulting in predictions which increasingly diverge from the observed behaviour. Figure 3 is an example from Site 1 of the different calibrated groundwater velocities obtained for different contaminants in different ports of two monitoring wells (MWS15 and MWS17).

6. MODEL PERFORMANCE

The performance of the models was variable. At Sites 1 and 3 none of the models performed well according to the qualitative criteria. At Site 2 the Environment Agency Remedial Targets Worksheet, P20 and DP1D performed reasonably well. The variable model performances were attributed to uncertainties in the datasets used to characterise complex site conditions. This variability made it difficult to incorporate full understanding of the site conditions into the site-specific conceptual site model (CSM) and fate and transport models.

While the overall performance of the models was relatively poor for the evaluated sites, use of the 1-D models provided a valuable insight into processes occurring at each site, in terms of the relative importance of double-porosity transport in the system and biodegradation processes. This provides necessary information to support the decision-making process and what emphasis to place on directing any further site investigation.

There are four key findings arising from the performance assessment, most relating to the fact that with sparse data the hydrogeological system cannot be characterised sufficiently well to have confidence in the modelling, and if the site is very well characterised the simple models are not capable of replicating the data:

1. Impact of poor characterisation of the groundwater flow system and fracture network – limited data on the aquifer hydrogeology and fracture network properties (fracture spacing, aperture and geometry) affected the model performance at Sites 2 and 3. At Site 1 the groundwater flow system was better understood but could not be fully incorporated into the contaminant fate and transport models.

2. Impact of poor source term definition – the source term is often poorly understood at a site and difficult to replicate in many models. At Site 1 the source term was relatively well understood, with release volumes and dates known. The inability to replicate source terms, both in terms of defining the source release times

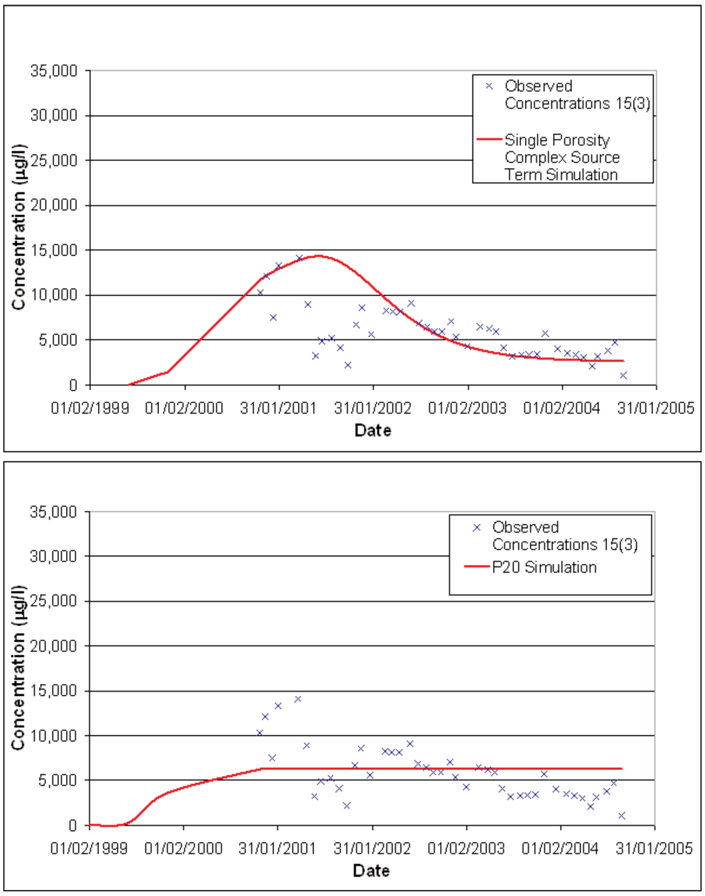

Fig.2: Calibration for benzene in BH15(3) at Site 1 using single porosity model with complex source term (top) and single porosity model with continuous source term (bottom)

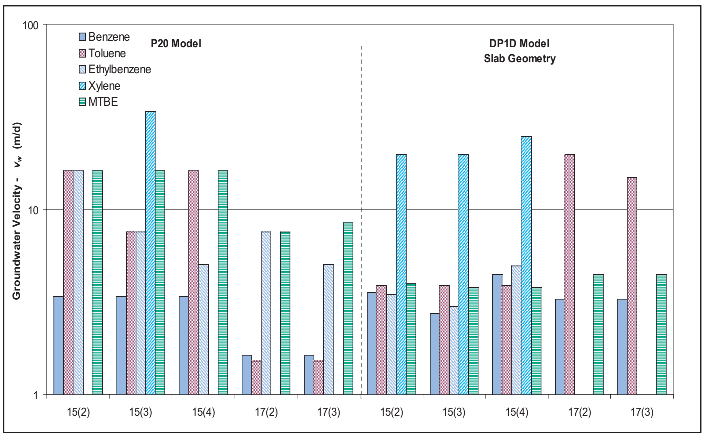

Fig.3: Groundwater velocities from Site 1 calibration

and volumes and simulating it within a model, impacts the model performance. However, despite better calibration using a complex source term model (Figure 2), the model performance was equally poor for both models used. It was therefore concluded that the influence of the groundwater flow system and fracture network were more important.

3. The TRAFRAP-WT model performed the best out of all of the models evaluated, with MODFLOW/MT3DMS having the worst performance. An example of this is presented in Figure 4. The results for the MODFLOW simulations highlighted the limitations of this single porosity flow model and quasi steady-state double porosity transport model in accurately representing double-porosity transport, which should always be considered.

4. The DP1D and TRAFRAP-WT models are based on a conceptual model of flow through fractures, while the P20 model simulates intergranular flow. However, the flow characterisation is essentially similar, being a darcian flux (calculated using Darcy's law in the P20 model or input directly in the DP1D model) through a mobile porosity (effective porosity in the P20 model or mobile porosity in the DP1D model). As a result, each model should show similar performance when groundwater flow is considered, which is the case (although the two models calibrate to different, but both feasible, groundwater velocities). However, the additional processes simulated (dispersion in the P20 model or double-porosity diffusion in DP1D) can produce multiple solutions, some of which are incorrect and lead to poor model performance. One way of establishing which model conceptualisation would be most accurate is to undertake tracer testing to estimate groundwater and contaminant velocity directly.

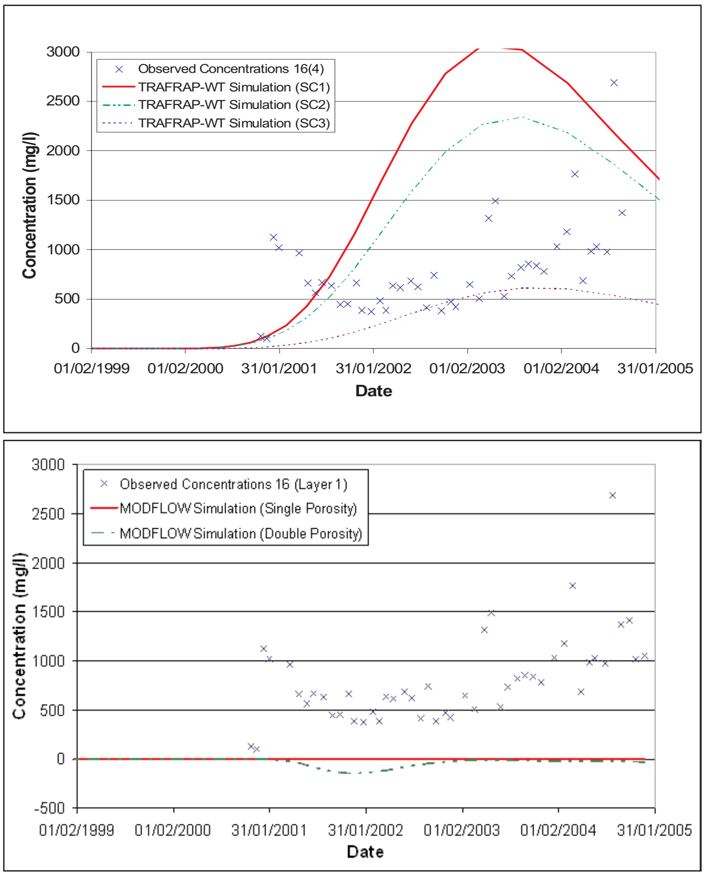

Fig.4: Performance of TRAFRAP-WT (3 scenarios) and MODFLOW/MT3DMS at Site 1 at BH16(4) for MTBE

7. MODELLING GUIDANCE

7.1 Model Selection

A number of important groundwater flow and solute transport processes occur in the Chalk aquifer:

- a transient groundwater flow regime, complicated by the presence of preferential pathways (fractures);
- complex fracture flow interactions, leading to mechanical dispersion;
- double-porosity diffusion between the fractures and matrix; and
- biodegradation controlled by the availability of electron acceptors (oxidants) and biomass.

While the results of modelling contaminant fate and transport in the Chalk aquifer must be treated with caution, the application of models can provide strong supporting evidence for the decision-making process. Particularly, application of models with simple flow fields (i.e. DP1D and PHREEQC) can serve as powerful tools to improve understanding of natural attenuation processes (i.e. double-porosity diffusion with the DP1D model and biodegradation with the PHREEQC model). However, limitations in representing the aquifer system, deduced from the site characterisation, requires that the modelling exercise is supported by an uncertainty analysis that focuses on the least constrained parameter inputs.

Double-porosity diffusion in the Chalk aquifer has two key effects on contaminant transport:

- diffusion of contaminants from the fracture to the matrix delays the contaminant arrival; and
- until diffusive equilibrium is reached, diffusion of contaminants from the matrix to the fracture will increase the contaminant concentration in the fracture.

The single porosity models, using dispersion as a proxy for double porosity will fail to adequately represent these processes. The first effect, delaying the contaminant breakthrough, will be limited in certain circumstances (e.g. short groundwater flow path, large fracture apertures, and rapid groundwater flow). As a result single porosity models may then be used to predict contaminant arrival times under these conditions, provided this is justified by the CSM and site characterisation. The uncertainty in determining groundwater flow velocities will require that sufficient characterisation of groundwater flow be undertaken prior to the application of these models.

Single porosity models could also be considered appropriate for simulating long-term contaminant concentrations, under steady-state conditions (i.e. when the source term is considered to be constant). However, predictions of long-term contaminant concentrations made using single porosity models are likely to be highly non-conservative where the source term is declining, due to dispersion and biodegradation, or is removed entirely (e.g. through remediation). Furthermore, the difficulties in calibrating single porosity models indicate that predictions made with these models are likely to be highly uncertain and the results should be treated with caution.

Characterisation and representation of the source term in a model is important to understand the long-term behaviour of a plume. It is difficult to justify the use of a highly complex source term in a model, considering the other uncertainties in the contaminant fate and transport processes. Some representation of the long-term evolution of the source, however, such as a declining source term in the model, provides a markedly better representation of the actual system, and hence the temporal evolution of contaminant concentrations.

In summary, the following model selection recommendations can be made:

- 1-D double porosity models may be used for all other situations;
- models with a declining source term should be used where applicable; and
- models that characterise the flowpath in more than 1-D have limited benefit (and are less cost-effective) unless uncertainty in groundwater flow and transport behaviour can be substantially reduced through the site investigation techniques detailed in sections 8.1 and 8.2. Multi-dimensional models may be better able to represent complex groundwater flow regimes, however there must be sufficient data to support their use.

7.2 Modelling Methodologies

This study showed that there is significant uncertainty in outputs from fate and transport models, such that all modelling results need to be treated with a substantial amount of caution.

Validation of the model calibrations increases the confidence in the model results, or assists with the development of the models by identifying limitations in the CSM, which in turn identify further data requirements. In practice it is sensible to use all available data. However, the model validation process requires the exclusion of data from the data set used for calibration. A sensible approach to modelling for the purposes of risk assessment is presented in Figure 5.

8. SITE INVESTIGATION GUIDANCE

8.1 Groundwater Flow System

Understanding contaminant fate and transport in the Chalk aquifer requires the development of a highly detailed CSM. This should consider the geology, hydrogeology, contaminant distribution and relevant processes controlling contaminant behaviour at a level appropriate for the complexity of the problem. For

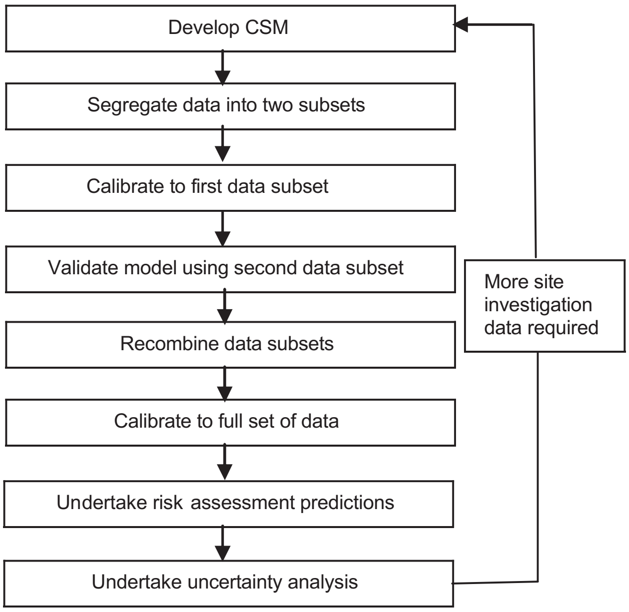

Fig.5: Recommended Modelling Methodology

sites where a detailed quantitative risk assessment is required that is likely to lead to remediation, the current standard of site investigation, with emphasis on limited intrusive investigation and assessment, provides insufficient information to develop a suitably detailed understanding of such sites.

It has become apparent during this project that high quality data provided through more detailed site investigations (e.g. Thornton and Wealthall, 2008) is required for robust quantitative risk assessment potentially leading to remediation, ideally comprising:

- *in situ* testing techniques such as natural-gradient tracer tests to better understand the distribution and connectivity of solute flow paths, as well as constrain groundwater velocity. Groundwater flow velocity can be a highly uncertain parameter when modelling contaminant fate and transport in double-porosity aquifers. Using conservative tracers in natural-gradient tracer tests, groundwater flow velocities as well as information relating to the double-porosity (fracture-matrix diffusion and interaction) behaviour of the system can be obtained;
- cored boreholes to obtain relevant information on the fracture network and matrix properties. These data will enable an initial assessment of the active flow zones as well as providing data on matrix porosity for double-porosity modelling;
- characterisation of vertical heterogeneity in aquifer hydrogeology and fracture-matrix solute interactions (e.g. using straddle-packer pumping tests and borehole dilution tests); and
- design of better monitoring well networks using multi-level groundwater samplers (with installation of transects in and down-gradient of the plume). This is necessary to characterise the plume geometry, identify significant flow paths for contaminant flux in the system and to understand the temporal variation in contaminant transport along the fracture system.

The project revealed that a detailed and representative CSM is fundamental to achieving good modelling results. In turn, site investigation provides the building blocks for the CSM refinement and model input data. Within the context of this project only, the optimum level of site investigation required is more than that undertaken at Sites 2 and 3 but slightly less intensive than undertaken at Site 1. This is discussed further in Wright et al, 2007.

8.2 Monitoring Regime

Design of the monitoring regime is also important, as sufficient data are required to fully characterise and therefore address the uncertainties relating to contaminant transport behaviour in the system:

- monitoring programmes should be undertaken over periods of one year or more at a suitable frequency to sufficiently understand groundwater flow variations with time. Potential causes of variation in groundwater flow that should be considered when deciding on monitoring frequency include seasonal and longer term (e.g. drought) effects, the operation of local abstractions, remediation and tidal effects; and
- detailed monitoring is required near the source to understand the influence of groundwater elevation and flow on source term concentrations and the timing of the contaminant release.

Although many of the simple 1-D models cannot replicate the variation in concentrations due to groundwater elevation and seasonal fluctuations in water table, it is recommended that the impact of these effects on contaminant concentrations is assessed to obtain a fuller understanding of the CSM.

8.3 Biodegradation Processes

Characterisation of biodegradation processes affecting contaminants in the aquifer can provide constraints on biodegradation rates applied in the models. Targeted analysis of groundwater samples collected from the fractures provides support for biodegradation activity (analysis should include at least dissolved O_2, NO_3^{2-} Fe^{2+}, Mn^{2+}, SO_4^{2-}, methane and total dissolved inorganic carbon).

Acknowledgements

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