Investigating the scale of structural controls on chlorinated hydrocarbon distributions in the fractured-porous unsaturated zone of a sandstone aquifer in the UK

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Abstract Contaminant migration behaviour in the unsaturated zone of a fractured porous aquifer is discussed in the context of a study site in Cheshire, UK. The site is situated on gently dipping sandstones, adjacent to a linear lagoon historically used to dispose of industrial wastes containing chlorinated solvents. Two cores of more than 100 m length were recovered and measurements of chlorinated hydrocarbons (CHCs), inorganic chemistry, lithology, fracturing and aquifer properties were made. The results show that selecting an appropriate vertical sampling density is crucial both to providing an understanding of contaminant pathways and distinguishing whether CHCs are present in the aqueous or non-aqueous phase. The spacing of such sampling should be on a similar scale to the heterogeneity that controls water and contaminant movement. For some sections of the Permo-Triassic aquifer, significant changes in lithology and permeability occur over vertical distances of less than 1 m and samples need to be collected at this interval, otherwise considerable resolution is lost, potentially leading to erroneous interpretation of data. At this site, although CHC concentrations were high, the consistent ratio of the two main components of the plume (tetrachloroethene and trichloroethene) provided evidence of movement in the aqueous phase rather than in dense non-aqueous phase liquid (DNAPL).

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Resumé Il est question de la migration de contaminants dans la zone non-saturée d'un aquifère poreux fracturé au niveau d'un site d'étude dans le Cheshire, UK. Celui-ci est situé sur des grès légèrement inclinés, adjacent à un lagon linéaire anciennement utilisé comme dépôt de déchets industriels contenant des solvants chlorés. Deux carottes de plus de 100 mètres de long ont été réalisées et des mesures et études ont été effectuées pour les hydrocarbones chlorés (CHCs), la chimie inorganique, la lithologie, la fracturation et les propriétés de l'aquifère. Les résultats montrent que pour comprendre les trajectories des contaminants et pour déterminer si les CHCs sont présents ou non dans la phase aqueuse, le choix d'une densité convenable pour le prélèvement vertical est essentiel. L'espacement des prélèvements devrait se baser sur la même échelle que l'hétérogénéité qui contrôle la circulation de l'eau et du contaminant. Au niveau de certaines parties de l'aquifère Permo-Triassique, il y a d'importants changements verticaux sur des distances de moins d'un mètre concernant la lithologie et al perméabilité; les échantillons doivent être collectés dans cet interval pour éviter de perdre en résolution, ce qui peut conduire à une interprétation erronée des données. Pour ce site, malgré des concentrations en CHC élevées, le rapport constant des deux principaux composants du panache (tétrachloroéthène et trichloéthène) révéla un mouvement en phase aqueuse plutôt qu'une DNAPL (Dense Non Aqueous Phase Liquid).

Resumen Se discute el comportamiento de la migración de contaminantes en la zona no saturada de un acuífero fracturado poroso en el contexto de un sitio estudiado en Cheshire, UK. El sitio está situado en arenizcas con pendiente suave, al lado de una laguna históricamente usada para desechos de basura industrial con contenido de solventes clorinados. Se recobraron dos núcleos de más de 100 m de longitud y se tomaron medidas de hidrocarburos clorinados (CHCs), química inorgánica, litología, fracturación y propiedades de los acuíferos. Los resultados muestran que la selección de una densidad apropriada de muestreo vertical es crucial tanto para proporcionar un entendimiento de las rutas de migración de contaminantes como para distinguir si existe la presencia de CHCs en la fase acuosa o no-acuosa. La separación de dicho muestreo debe ser de una escala similar a la heterogenidad que controla el movimiento de agua y de contaminantes. En

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algunas secciones del acuífero Permo-Triásico cambios importantes en la litología y la permeabilidad ocurren a distancias verticales de menos de 1 m y las muestras deben ser tomadas en este intervalo, o de otro modo se pierde una resolución considerable, potencialmente esto puede causar una interpretación incorrecta de los datos. En este sitio, a pesar de que las concentraciones de CHC eran altas, el ratio consistente de los dos componentes principales de la pluma (tetracloroetano y tricloroetano) proporciona evidencia de movimiento en la fase acuosa en lugar de DNAPL.

Keywords Chlorinated solvents · Sampling · Fractured rocks · Unsaturated zone · Dual-porosity

Introduction

Since the early 1980s, increasing attention in the industrialised countries of western Europe and North America has been given to the contamination of groundwater by a range of synthetic organic chemicals. Of particular concern have been the chlorinated hydrocarbons (CHCs) reflecting both their frequent and widespread occurrence in groundwater (Rivett et al. 1990a; NRC 1994; Moran and Davis 1998), and their physicochemical characteristics which make them especially troublesome contaminants in the subsurface. These characteristics include: low aqueous solubility with the potential to remain in the non-aqueous phase, persistence of some of the more highly chlorinated compounds under normal subsurface conditions, weak sorption by common aquifer materials and low permitted drinking-water guidelines (Aurand et al. 1981; Mercer and Cohen 1990; WHO 1998).

The liquid chlorinated solvents are commonly denser than water (an exception being vinyl chloride) and are often classed as dense non-aqueous phase liquids (DNAPLs). DNAPLs can sink through an aquifer and accumulate on poorly permeable horizons, slowly dissolving in groundwater to produce dissolved-phase plumes, which may adversely affect downstream users of groundwater. In fractured aquifers, DNAPL migration may be both rapid and localised, controlled largely by fracture aperture, interconnectivity and orientation. Accurate prediction of DNAPL movement in fractured rocks is likely to prove costly and be difficult, if not impossible to achieve (e.g. Toussaint and Weyer 1992a,b; Sudicky et al. 1998).

The Triassic Sherwood Sandstone, which is the most important aquifer in northern England and the west Midlands (Fig. 1), underlies areas with a long history of heavy industry, chemical manufacturing and metal processing. As a consequence of historical spillages around specific sources, contamination of the sandstone aquifer by CHCs is known to be both locally significant and widespread under some urban centres (Rivett et al. 1990b; Lawrence et al. 1992; Burston et al. 1993; Hooker et al. 1999) and others are assessed as being at risk (Tait et al. 2004).

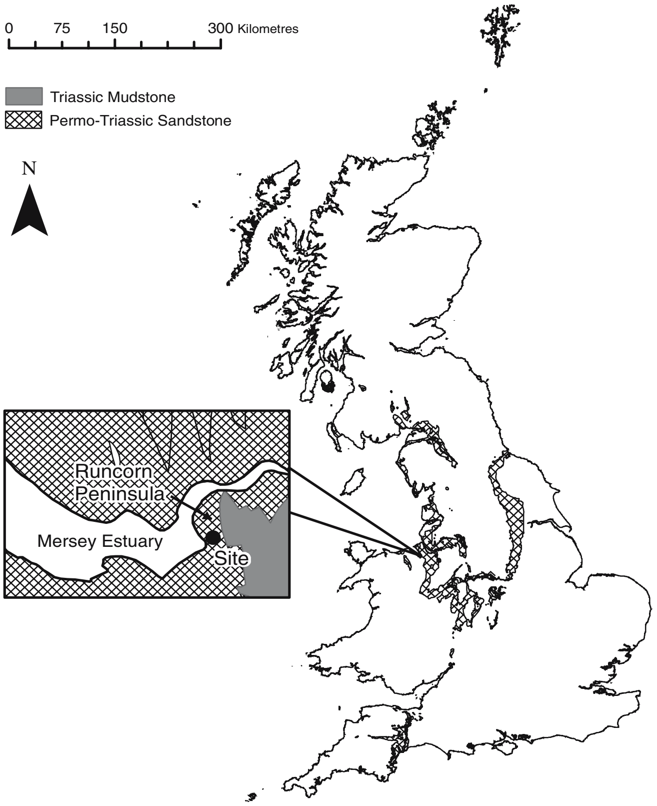

Fig. 1 Outcrop of the Permo-Triassic sandstones in Great Britain with inset showing site location

The sandstone commonly has a deep unsaturated zone frequently 10–30 m thick but which can be in excess of 50 m (Allen et al. 1997). Water movement in the unsaturated zone can be complex, with ponding on less permeable layers, potentially giving rise to perched water tables and lateral flow above less permeable layers, particularly where recharge is high.

Assessment of the risk posed to the environment and to long-term groundwater users by a contaminated site, particularly where DNAPLs may have been used, often requires characterisation of contaminant distribution close to the source. Core drilling and detailed porewater sampling in conjunction with evaluation of aquifer characteristics and heterogeneity can help to provide an understanding of contaminant processes and assessment of whether DNAPL was, or is, present. Such investigations are costly and can potentially exacerbate the situation by cross-contamination. Therefore invasive techniques (e.g. drilling) need to be optimised and the amount of information extracted from any borehole maximised.

The purpose of this paper is to discuss contaminant migration behaviour in the unsaturated zone of the Sherwood Sandstone aquifer and to consider the requirements for successful investigation methodologies. A case study is presented which shows that selecting an appropriate density of sampling is crucial both to providing an understanding of contaminant pathways and distinguishing whether CHCs are present predominantly in the aqueous or non-aqueous phase.

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Hydrogeology of the Sherwood Sandstone Group

The Permo-Triassic sandstones of the UK, of which the Sherwood Sandstone Group constitutes a major part (Table 1), form the second-most important aquifer after the Chalk, in terms of quantities of water abstracted, but are the most important in terms of volumes of groundwater stored (Allen et al. 1997).

The Sherwood Sandstone Group is largely of fluviatile origin, deposited by a braided river system, but locally aeolian deposits also occur. The total thickness of the sequence can be up to several hundreds of metres. The predominant lithology is sandstone, although some conglomerates, siltstones and mudstones are usually present (Allen et al. 1997). Fining-upwards cycles are common in the fluvial deposits of the upper part of the sandstones. Each cycle may vary from one to several metres thick; the basal member of the cycle is usually represented by a coarse sandstone or conglomerate which progressively fines upwards to a fine-grained sandstone, siltstone or mudstone (Walker and Cant 1984). The aeolian sandstones tend to be more homogeneous, both laterally and vertically.

Interbedded sandstone-mudstone successions can be considered as falling into three main types, depending on geometry of the sandstones, the ratio of sandstone to mudstone present in the succession, the interconnectivity of the sandstones and the lateral continuity of the mudstones. In decreasing order of connectivity of sandstones (increasing amounts of mudstone) these types are:

- Layer-cake
- Jigsaw
- Labyrinth (not considered further since it is not normally present in the Sherwood Sandstone)

The characteristics of the layer cake and jigsaw types in cross-section are illustrated in Fig. 2. The importance of these characteristics is that they can be used as models to aid prediction of potential fluid flow through the succession. For example, the layer-cake architecture has laterally continuous mudstone beds that may restrict vertical migration of fluids; any fluid flow will be parallel to the bedding. Conversely, mudstones within the jigsaw architectural model are discontinuous and do not form barriers to fluid flow, although they can locally form baffles. Fluid flow within this type of succession can be orthogonal to bedding.

Table 1 Stratigraphy of the Permo-Triassic sandstones of the Cheshire Basin

Period	Group	Local Formation
Triassic	Mercia Mudstone	
	Sherwood Sandstone	Helsby Sandstone Wilmslow Sandstone Chester Pebble Beds Kinnerton Sandstone
Permian		(Manchester Marl) Collyhurst Sandstone

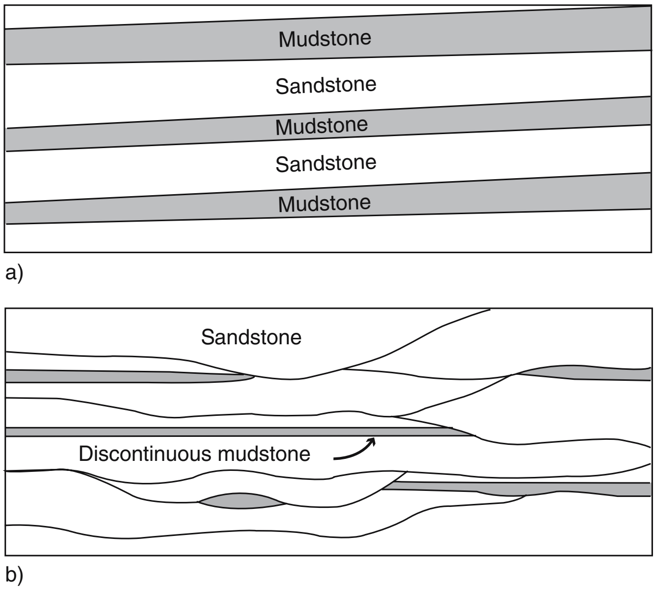

Fig. 2 Architectural models of interbedded sandstone–mudstone. **a** Layer-cake where layering is distinct with marked continuity and gradual thickness changes, and **b** jigsaw where different sandstone bodies fit together without major gaps and occasional low-permeability mudstones act as local baffles but not complete barriers

The upper part of the Sherwood Sandstone consists of mainly jigsaw architecture. In the Helsby Sandstone (Table 1), sheet and lenticular channel sand bodies interbedded with laterally discontinuous mudstone beds form the majority of the succession. Major mudstone prone intervals within these may have layer-cake architecture. The underlying Wilmslow Sandstone is aeolian and also has jigsaw architecture although mudstones are less common.

Aquifer transmissivities for the sandstones range from 1 to 5,000 m^2/day (median 189 m^2/day) and well yields of 5,000 m^3/day are not uncommon (Allen et al. 1997). These yields reflect both the moderate to high hydraulic conductivity of the sandstones and the considerable thickness of the aquifer. For the sandstones, hydraulic conductivities can be up to 15 m/day but are much lower for the finer-grained or more-cemented lithologies. The permeability of the mudstone horizons cannot be measured in the laboratory since a coherent plug cannot be cut, but it is assumed to be several orders of magnitude less than the sandstones. The sandstones possess primary porosities of 15–35%, which provide considerable volumes of groundwater storage. Dominant pore throat sizes vary from 0.1 to 100 µm so that within the unsaturated zone the larger pores are likely to be drained (and thus air-filled), whilst the smaller pores will retain their water (Price 1977; Allen et al. 1997; Bloomfield et al. 2001).

The sandstones are also cut by fractures; the spacing between fractures is variable but is often relatively infrequent, on a scale of metres, particularly for vertical fractures (Allen et al. 1998). The contribution of these fractures overall to aquifer transmissivity is less clear. Certainly investigations in the Sherwood Sandstone have shown that the fracture flow can be the predominant contributor to the groundwater inflow into individual boreholes (Walthall and Ingram 1981; Price et al. 1982). However, other studies have shown that for flow at the regional scale, it is matrix flow that dominates (Walthall and Campbell 1986; Allen et al. 1997). These apparently contradictory observations are usually explained by assuming that the fracturing is largely localised and possibly associated with sand-infill being washed into major abstraction boreholes (Price 2003). As a consequence, flow at the regional scale is controlled by the matrix permeability.

Contaminant migration and controls in the unsaturated zone

At contaminated sites, the CHCs may be present both as DNAPL and aqueous phase. For the assessment of fate and transport, it is necessary to be able to distinguish between these phases, since the aqueous phase will migrate with regional groundwater flow, whereas DNAPL migration at the local scale is typically controlled by preferential pathways such as fractures and large diameter interconnected pores.

The chlorinated solvents, in the non-aqueous phase are non-wetting fluids with respect to water and, in a water-wet porous medium, will be confined to the larger openings (Keuper et al. 1989). Lawrence et al. (1992) estimated the likely excess pressure required for tetrachloroethene (perchloroethylene, PCE) to invade (displace water from) saturated Permo-Triassic sandstones for a range of apertures. This suggested that excess heads of only a few tens of centimetres of DNAPL would be required to displace water from the large pore apertures (10–50 μm) or several meters for the smaller pore apertures (1–10 μm). More recent research (Gooddy et al. 2002) suggests that for industrial-grade PCE, the contact angle in water–sandstone systems is higher than previously reported. As a consequence, the excess pressure required for such PCE to displace water from sandstone is lower, and excess heads of less than 10 cm may be sufficient to displace water from pores of 1 μm aperture.

Two questions arise when considering DNAPL movement through the unsaturated zone of the Permo-Triassic aquifer: Is DNAPL movement predominantly through fractures or the matrix and how do the various lithologies influence DNAPL movement? Based on the characteristics of the fracturing in the Permo-Triassic Sandstones in the vicinity of the study area (Table 1), migration through the matrix is thought to be predominant because:

- The major vertical or subvertical fracture spacing is large (10–20 m); in consequence the contaminant would be in contact with a much greater area of matrix than fracture since typically the ratio of matrix to fracture porosity is greater than 50:1 (the fracture porosity is likely to be as low as 0.1–0.5% and the matrix porosity to exceed 25%)
- The majority of vertical or subvertical fractures are thought to be sediment-filled which considerably reduces the permeability contrast with the matrix
- Many vertical or subvertical fractures are discontinuous and are restricted to individual beds and are therefore less than 2 m in length

In addition, within the unsaturated zone of the sandstones, the larger pores (and fractures) will have been drained and DNAPL will migrate preferentially through these air-filled voids. Moisture content measurements on core obtained during drilling indicate that about 30% of the pores are air-filled.

The siltstone and mudstone layers in the upper part of the Sherwood Sandstone will be mostly water-saturated because of their much smaller pore neck size. As a consequence, these finer lithologies will act as barriers to downward movement of DNAPL (Keller et al. 2000). However, in fluvial sandstones with typical jigsaw architecture, downward movement of DNAPL may be possible because the DNAPL can flow around the ‘barrier’ (Fig. 2). Nevertheless, some lateral movement can be anticipated. In sandstones with layer-cake architecture, downward movement of DNAPL is more problematic and significant lateral spreading is probable, although downward migration may be possible where vertical fractures cut through the less permeable mudstone layers (Reynolds and Kueper 2004).

Once the main body of DNAPL has passed through the rock, some will remain infilling some of the pores and fracture spaces. This retained DNAPL is usually referred to as residual. In granular aquifers, residual can occupy more than 30% of the total pore volume (Hunt et al. 1988), which corresponds to about 5–10% of the rock volume in the case of the Sherwood Sandstone. However, in fractured bedrock aquifers, the residual will occupy a much smaller fraction of the rock volume (Mackay and Cherry 1989). This residual remains heterogeneously distributed within the unsaturated zone in response to its structure following the downward passage of the main DNAPL body (Poulsen and Keuper 1992) and acts as a secondary or subsurface ‘DNAPL source’ of the contaminant (Lawrence et al. 1992). The mass of residual DNAPL will be reduced by processes of dissolution, diffusion, advection and volatilisation. Degradation of some CHCs, particularly perchloroethylene (PCE), trichloroethene (TCE) and their daughter products, can be negligible, particularly in aerobic environments such as the unsaturated zone. These processes are slow and residual is likely to remain in the unsaturated zone for years or decades (Parker et al. 1994; Abriola and Bradford 1998).

Dissolution of residual by subsequent infiltration will produce a dissolved phase plume within the unsaturated zone. Water movement in the unsaturated sandstones is likely to be complex given the wide range of lithotypes and their geometries. Under high hydraulic surcharging water is likely to follow a similar pathway to DNAPL, spreading laterally across less permeable layers, due to the limited water infiltration capacity of these layers.

Data requirements for evaluating contaminant distribution

Evaluating contaminant distribution within the unsaturated zone presents special difficulties, in part because of the difficulty and cost of obtaining water samples. However, core drilling and analysis of fluids present in the rock can provide an insight into the contaminant distribution (Lawrence et al. 1990). Further, where this understanding is combined with information on geological heterogeneity and fracturing, the likely pathways through the unsaturated zone may be inferred.

In this respect, the issue of sample density and data aggregation is of crucial importance and this has been well established for numbers and spatial distribution of sampling points (e.g. Grabow et al. 1993; Vucetic and Obradovic 2000). Where funds are limited, a balanced approach must be taken between too few and too many samples. Sampling at too coarse a scale will limit costs, but may result in missing important data and the drawing of erroneous conclusions. Very large numbers of samples will increase the cost of the investigation both in terms of analytical cost and in sample selection and preparation. The latter may limit drilling progress significantly where large numbers of samples are involved because it is advisable to analyse for DNAPL-forming contaminants on-site. The results are needed to guide drilling progress in order to avoid possible cross-contamination problems such as DNAPL migration to a lower uncontaminated stratum using the new pathway provided by the open borehole.

It is suggested that a sensible guideline should be that a sampling frequency that corresponds to the scale of lithological heterogeneity should be used. For example, if lithological changes are occurring over 0.1 m intervals, then sampling intervals should be of a similar order. If there is no a priori knowledge of the scale of lithological heterogeneity at the site, then it may be hard to determine the correct scale at which to sample. Under such circumstances, it may be necessary to drill an exploratory lithological borehole in a nearby uncontaminated location to gain the required information.

Where contaminant transport by vertical fractures may be important, angled or inclined boreholes are likely to be more effective. This is because vertical boreholes are unlikely to intercept these fractures especially where the fracture spacing is typically of the order of metres.

The study site

Site description

The study site was an old, disused sandstone quarry located on the Runcorn Peninsula, Cheshire. The quarry was about 35 m deep and had been used to dispose of contaminated lime slurries during the period 1935–1951 (ENDS 2000). The contaminants included chlorinated hydrocarbons which were likely to have been present in both the dissolved and non-aqueous phases. The main chlorinated hydrocarbons included trichloroethene (TCE) and PCE. Large volumes of supernatant liquid drained out of the quarry into the sandstone during the period when the slurries were being disposed, leaving behind a thick sludge. Once the quarry was nearly filled with sludge, it was covered with fly ash and grassed over.

Permo-Triassic rocks of the upper part of the Sherwood Sandstone sequence, the Helsby and Wilmslow Sandstone Formations, underlie the site (Table 1), the former comprising cemented fluvial channel-succession deposits which were originally quarried for building stone. Local lithostratigraphic information for the Helsby Sandstone Formation, including the scale of vertical and lateral lithological variations as observed in the former quarry walls prior to infilling was provided by Hull (1982), Maidwell (1914, 1915) and Wray (1937). The lithologies exposed at the outcrop near to the site consist of soft to well-consolidated sandstones with subordinate mudstones and flaggy sandstones.

Mapping of the fractures in local road cuttings and an old tunnel beneath part of the site, showed that in this part of the sandstones, major vertical fractures cutting across the bedding were widely spaced (10–20 m, Table 2). These fractures tended to be about 5 mm across and were usually filled with loose uncemented but compacted sediment (Wealthall et al. 2001). Other smaller vertical and cross-bedding fractures tended to be of limited aperture and to be restricted to individual beds. Bedding plane fractures were also generally narrow, but may have been laterally extensive with the largest associated with pronounced lithological changes.The unsaturated zone is up to 75 m thick with the water table about 35 m below the base of the quarry.

Site investigation methodology

The overall purpose of the site investigation was to provide data to enable an assessment of the risk posed to the environment by the chemicals and slurries disposed in

Table 2 Summary of fracture characteristics for the Sherwood Sandstones of the Runcorn peninsula (from Bloomfield, 1996, personal communication and Wealthall et al. 2001)

Fracture orientation	Type	Spacing (m)	Aperture (mm)	Length (m)
NNW-SSE	Dominant subvertical multilayer cross-cutting outcrop	10–20	0.2–27	>5
NNW-SSE	Minor, subvertical	2.5	<1	<2
WSW-ENE	Minor, subvertical	0.1–0.3	<1	<2
Horizontal	Bedding plane	0.1–0.3	<1	<5
Horizontal	Cross-bedding	0.1–0.3	<1	<0.3

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the quarry. The approach adopted was to obtain detailed pore-fluid concentration profiles of organic and inorganic components in the unsaturated zone. The purpose of this paper is to demonstrate how such detailed profiles can provide insight into contaminant migration and how the sampling frequency affects the interpretation. Only data relevant to these aspects of the study are presented here.

Two cored boreholes were drilled adjacent to the quarry using a 100 mm-diameter mud-flush rotary coring method, one vertical and the other inclined. The inclined borehole penetrated the strata beneath the quarry floor. Both boreholes were drilled to a depth of about 100 m, the inclined borehole (angled at 45° to the horizontal) just reached the water table, whilst the vertical borehole penetrated some 20 m into the saturated zone.

A mud-flush method was selected in order to enable inclined drilling and to prevent the mobilisation of DNAPL, should a 'pool' be penetrated (Sterling et al. 2005). It also had the additional benefit of minimising volatile losses from the core. Large amounts of mud were required where major vertical fractures were intersected by the inclined hole. The extent of invasion of the core by mud was assessed by adding a lithium bromide tracer to each batch of drilling mud and subsequently analysing samples of both the mud and porewaters for lithium.

A continuous lithological log was made for each length of core as soon as it was available. From this log, a lithotype code was allocated to each metre of core corresponding to the average lithology. The number of low-permeability bands per metre was also calculated. All fractures were also logged, regardless of whether they may have been drilling-induced, and the fracture density per metre calculated. The orientation of the fractures in the inclined hole was determined where it was possible to discern bedding laminations within the core.

A detailed programme of core sampling and analysis was carried out (Table 3). After core logging, one 5-g core sample for CHCs from each sampling interval was weighed directly into a headspace vial, ultrapure water was added and the vial was sealed directly (Stuart 1991). Expected variations in aquifer properties on the submetre scale suggested that a similar vertical sampling interval would be appropriate and a spacing of 3 per metre was selected. This should account for heterogeneities that occur at a 2–4-m scale, corresponding to different channel units, and at 10s of cm, corresponding to different lithotypes. However, it would not distinguish changes at the mm to cm scale. Extra samples were collected close to specific vertical fractures in the inclined borehole to determine if CHC concentrations were enhanced.

Table 3 Summary of samples collected during drilling

Sample type	Analyte	Sampling interval (m)	On-site analysis
Rock	CHC	0.3	Yes
	Semi-volatiles	5	No
	Porosity, permeability, pore size distribution	2	No
Porewater	SEC, alkalinity, pH	1	Yes
	Inorganics	1	No
	Total organic carbon	5	No

Analysis for CHCs was undertaken on site to allow rapid identification of the presence of DNAPL. It was considered that if DNAPL were present either as 'residual' within the sandstone matrix or as a 'pool', it could be recognised by an 'apparent concentration' (mass of CHC per volume of porewater calculated from solid sample weight and its moisture content) greater than the aqueous solubility (Fig. 3). It was thought that if DNAPL had migrated through only the fractures, then any residual present might now have disappeared, given the low residual saturation in fractures compared with the matrix and the elapsed time between possible DNAPL migration and the investigation. From measurements of diffusion rates, disappearance times for DNAPLs are expected to be in the order of years for TCE and decades for PCE (Parker et al. 1994). However, even if residual saturation had disappeared, areas of higher aqueous concentrations surrounding fractures might be anticipated. Core samples for physical properties were sealed in plastic bags and subsampled and analysed in the laboratory.

Porewater for determination of inorganic species was extracted by refrigerated high-speed centrifugation on-site (Edmunds and Bath 1976). pH was measured and alkalinity was determined immediately on-site by autotitration with dilute sulphuric acid. Specific electrical conductance (SEC) was measured using a digital meter. The remaining sample was divided and preserved as appropriate for cations, anions and dissolved organic carbon for later laboratory determination.

Results

The results indicated that groundwater in both the saturated and unsaturated zones contained both CHCs and sodium/calcium chloride well above the baseline concentrations observed by Edmunds et al. (1989). The unsaturated zone concentration profile of both the CHCs and inorganic compounds showed very large changes in concentration over short vertical distances. The high frequency of sampling allowed the chemical data (organic and inorganic) to be compared and to be related to the physical characteristics of the rock matrix.

There was generally very good qualitative correspondence between CHCs, SEC, the various lithological units and the density of fracturing, although there were a few exceptions as might be anticipated in a complex natural system. One such relationship is illustrated in Fig. 4 where low PCE concentrations and SEC were measured in parts of the aquifer where clean sandstones layers were delineated by core and gamma ray geophysical-borehole logging. High contaminant concentrations in the porewaters appear to correspond with parts of the aquifer where mudstone and more-complex silty layers were delineated, perhaps indicating a degree of ponding on and diffusion into mudstone horizons (e.g. at 28, 21, 7, 1

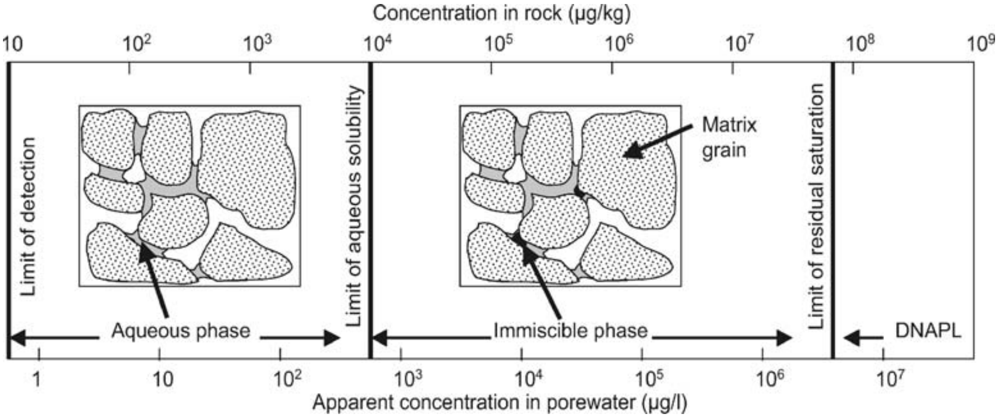

Fig. 3 Ranges of apparent porewater concentrations produced by aqueous phase, DNAPL residual saturation and free DNAPL

and −2 m OD). The differing sampling interval and methodologies used for the various parameters makes a statistical analysis difficult. The results of the limited more-detailed sampling fell within the concentration range obtained from the 3-per-metre sampling and could not be related to small-scale lithological variability.

Geological logging indicated that the permeability of the sandstones (both vertical and horizontal) was likely to vary by several orders of magnitude over depths of <1 m. Laboratory measurements for rock permeability and porosity were usually only made on samples at 2-m intervals (Fig. 5). Although more detailed information was gained from an assessment of the number of poorly permeable bands per metre. The latter information is not presented but related well with both the permeability and with CHC concentrations. Measurements using a field permeameter on a short section of sandstone core from a nearby borehole showed that sandstone permeability was in fact very variable on the cm to 10s cm scale.

Fracturing is often, but not always, related to lithology, since many of the fractures appear to be bedding plane partings, which occur more frequently in the interbedded flaggy, finer sandstones and mudstones. The fracture density, as observed in the two rock cores, is also compared with CHC concentrations in Fig. 5, generally with reasonably good correspondence.

In the inclined borehole, the results of detailed subsampling close to the surfaces of identified vertical fractures showed no evidence of enhanced concentrations of CHCs, supporting the likelihood of past rapid move-

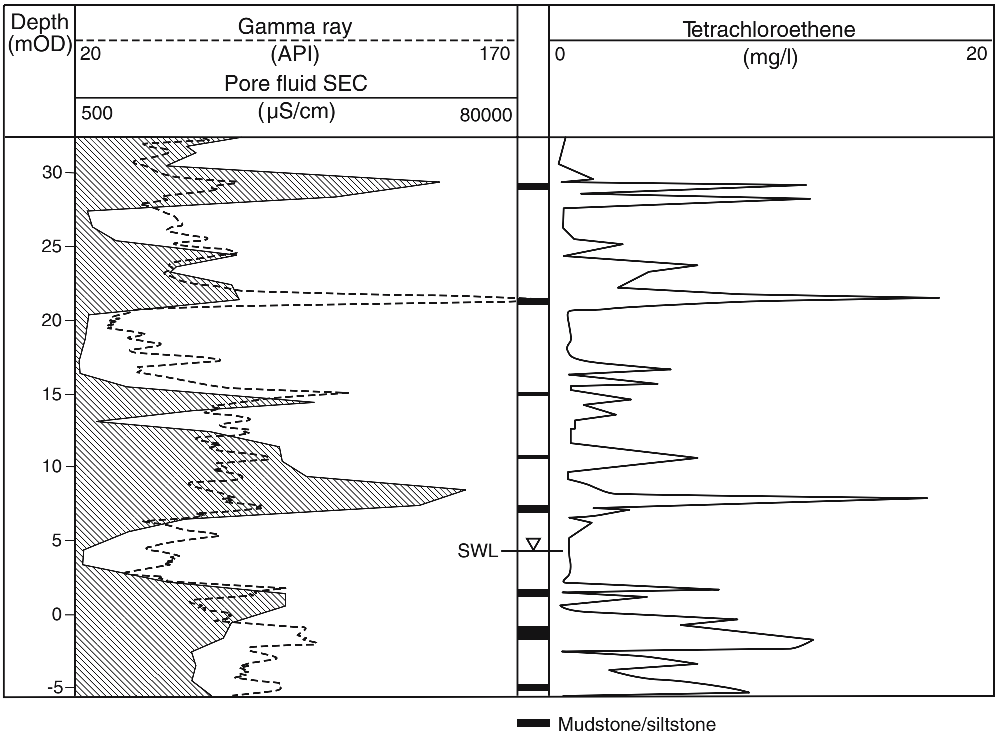

Fig. 4 Section of gamma ray geophysical log (*dashed line*) of vertical borehole compared with concentrations of PCE (tetrachloroethene) and porewater conductivity (SEC, *shaded region*)

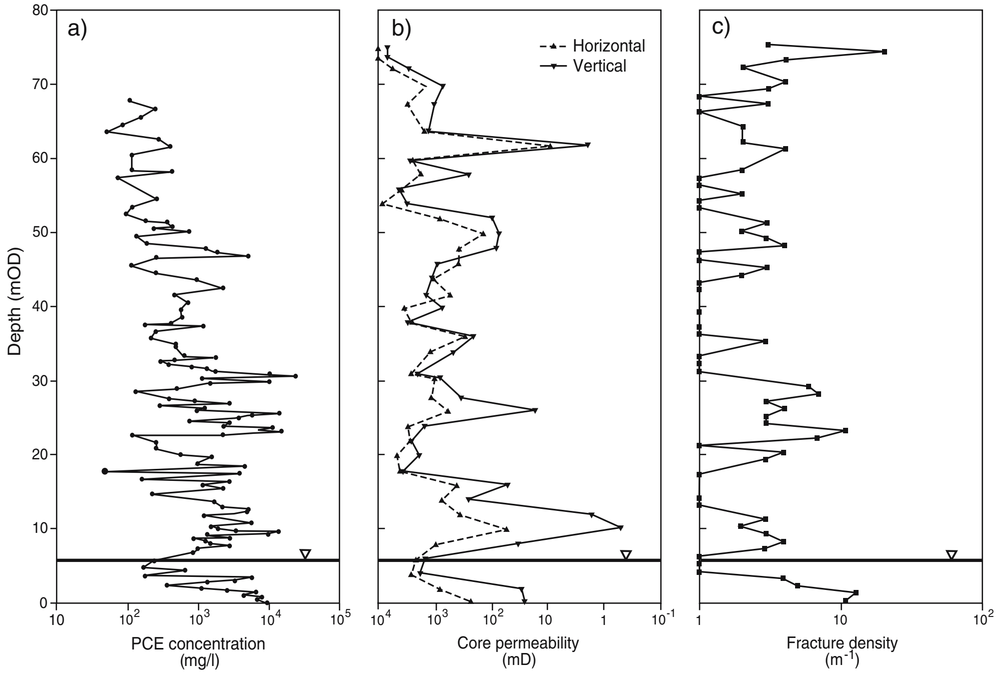

Fig. 5 Comparison of **a** PCE concentration with **b** core permeability and **c** fracture distribution in vertical borehole. The milliDarcy (mD) is the most commonly used unit of intrinsic rock permeability, approximately equivalent to 10^{-3} μm^{-2}

ment of non-aqueous or immiscible phase contaminants within the fractures. The CHCs are believed to have migrated through the sandstones as the aqueous phase. This is based on three independent lines of evidence:

1. Concentrations of the main CHCs are generally below their aqueous solubility. The aqueous solubility of individual CHCs depends on both the total concentration of salts present in the solution and the total concentration of other CHCs present. PCE solubility in brine was calculated using the relationship described by Horvath (1982):

   $$C_S = C_W \times 10^{(-\mu S)}$$

   where C_S is the solubility in salt solution, C_W is the aqueous solubility, μ is the salt coefficient and S is the salt concentration. Assuming a salt coefficient of 0.081 L/mol (Wilkinson, 1998, personal communication), PCE solubility was reduced from 150 mg/L (Mercer and Cohen 1990) to a minimum of 125 mg/L by the maximum chloride detected in the zone below the base of the quarry (34 g/L). The effective solubility due to the presence of other CHCs can be approximated using Raoult's Law (Broholm and Feenstra 1995):

   $$C_m = C_w \times m$$

   where C_m is the solubility of an individual component, C_w is the aqueous solubility and m is the molar fraction of the component in the mixture. Assuming that TCE and PCE are the main CHC components and that there is an average molar ratio of PCE to TCE of 0.71 (Fig. 6; slope of graph 1.11× molar weight of PCE/molar weight of TCE), the molar fraction of PCE is 0.41 (0.71/1+0.71). This further reduces the effective PCE solubility to about 51 mg/L (125×0.41). However, it should be recognised that there is some uncertainty in both the aqueous solubility of PCE and its modification due to the presence of high salinity and other CHCs. Figure 7 compares the PCE concentrations detected in both boreholes with this calculated effective solubility. Overall the PCE concentrations are well within the aqueous limits with only a few peak concentrations

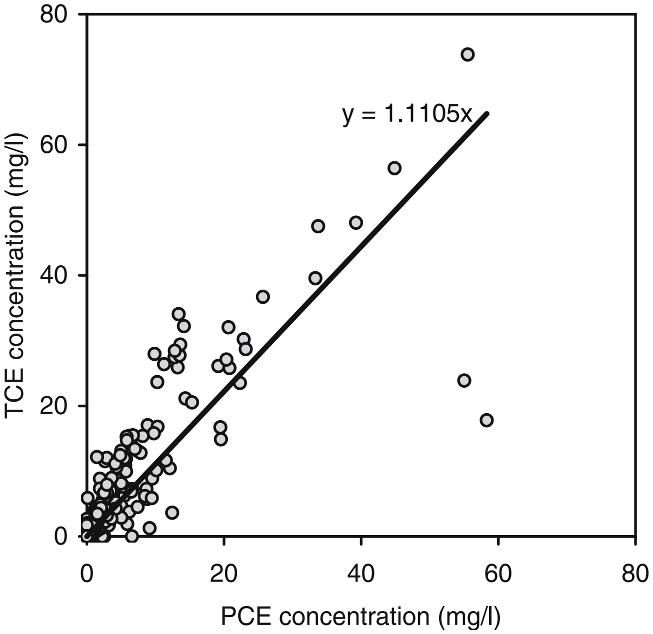

Fig. 6 Scatter plot of PCE and TCE concentrations in vertical and inclined boreholes

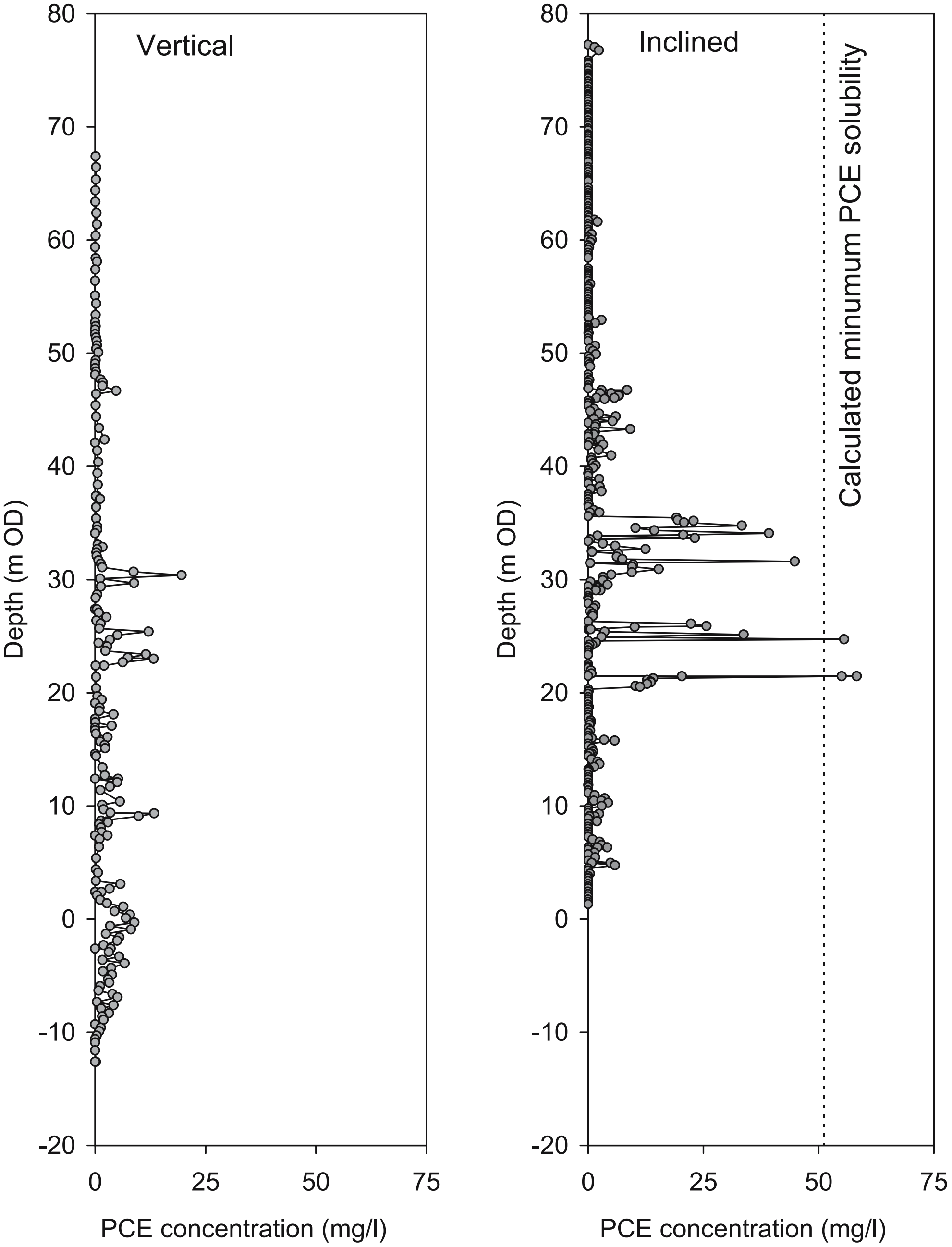

Fig. 7 PCE profiles in vertical and inclined boreholes and calculated PCE solubility in brine

exceeding the estimated effective solubility limit for PCE. Direct comparison of the results with the solubility estimates suggests that migration of a small amount of DNAPL into the unsaturated zone underneath the quarry cannot be ruled out. However, since the effective solubility is only an approximation, peak concentrations may in fact be within the aqueous limit.Concentrations of >10% of the relevant aqueous solubility are normally considered as evidence of the presence in the aquifer, at some stage, of the immiscible phase (Hunt et al. 1988). This is not useful here since it is known that the immiscible phase was originally present in the quarry fill and this would not be distinguished from immiscible phase in the unsaturated zone.

2. The close coincidence of high concentrations of CHCs and inorganic species such as chloride, calcium and sodium, suggests that the organic and inorganic components migrated along the same pathways. There are no instances of high CHCs in the absence of high inorganics. A number of sharp peaks at between 20 and 35 m OD (outer diameter) in the inclined borehole indicate either spreading beneath the quarry floor across low permeability layers or fingering via vertical or subvertical fractures (Fig. 5). These mechanisms

cannot be easily distinguished by a single borehole at 45°. However, the coincidence of peaks with low permeability layers and the lack of CHC enhancement close to fractures suggests the former.

3. The ratio of TCE:PCE is remarkably constant throughout the profiles (Fig. 6), which is consistent with a large uniform source, but not necessarily of the aqueous phase. Had the CHCs migrated out of the quarry as a series of separate DNAPLs, different proportions are likely to have been present. The two samples with the highest CHC concentration have a different TCE:PCE ratio. This may be because they have been derived from DNAPL, although differences in the composition of the waste stream may also be a factor.

The overall conclusion is that high concentrations of CHCs and inorganics are almost always associated with less permeable bands in the profile, consistent with lateral migration of fluids above these layers and possibly along bedding plane fractures. It is suggested that this association, in combination with downward movement through sandstones where mudstones have pinched out or are discontinuous, leads to the distribution in the subsurface shown schematically in Fig. 8. Both vertical and inclined boreholes intersect frequent horizontal low-permeability layers and bedding plane fractures. Even within individual channel units fine micaceous sandstones may be present and are likely to act as barriers. These low permeability units form the 'floors' of the invaded matrix. Downward migration continues either where the low-permeability layers 'pinch out', or possibly where significant vertical fractures are present, producing 'pillars' of contaminated matrix. The spacing of these pillars is not known but is assumed to be at least 10–20 m. This means that the likelihood of intersection by a vertical borehole is very small and that an inclined hole may only intersect one or two. In the case study, all peaks in the CHC or inorganic profiles are associated with low-permeability layers and there are none which could be unequivocally attributed to vertical migration.

Sampling density: implications for data interpretation

Having made the above interpretations based on a sampling density for CHCs of 3 per vertical metre, it is useful to assess what impact different sampling frequencies and regimes would have had on data interpretation and subsequent conclusions. Four alternative scenarios were considered:

- Bulked samples (samples made up from subsamples within a given depth range) at 2-m intervals
- Bulked samples at 5-m intervals
- Spot samples (i.e. from discrete 1-cm depth range) at 2-m intervals
- Spot samples at 5-m intervals

Bulk samples

For convenience, all the samples in the dataset shown in Fig. 9a were used (equivalent to spot samples at 0.3 m intervals). For each interval, all the results were combined into an 'average value' for that interval. For 2-m intervals, this represented usually six subsamples. The results are plotted for 2 and 5-m intervals in Fig. 9b and c. It can be seen from Fig. 9b that when samples are bulked over 2-m intervals, the resolution of individual peaks is lost although the main contaminated zones are identified. It would be impossible from this dataset alone to determine the role of lithology on contaminant movement. When the interval is increased to 5 m, the resolution is diminished further but the main zones can still be identified.

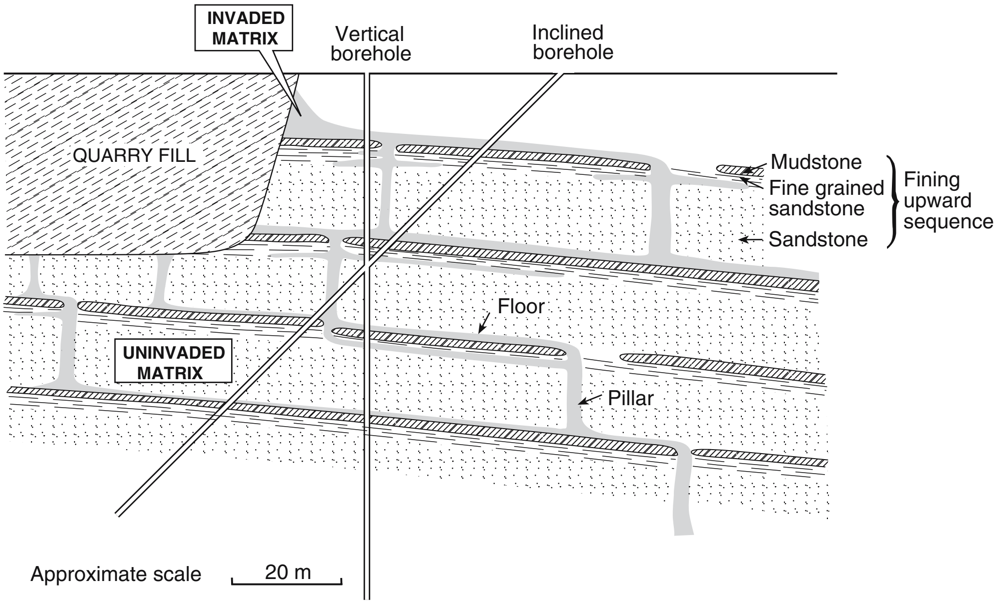

Fig. 8 Conceptual model of residual contamination in the Sherwood Sandstone forming 'pillars' and 'floors' of contaminated matrix

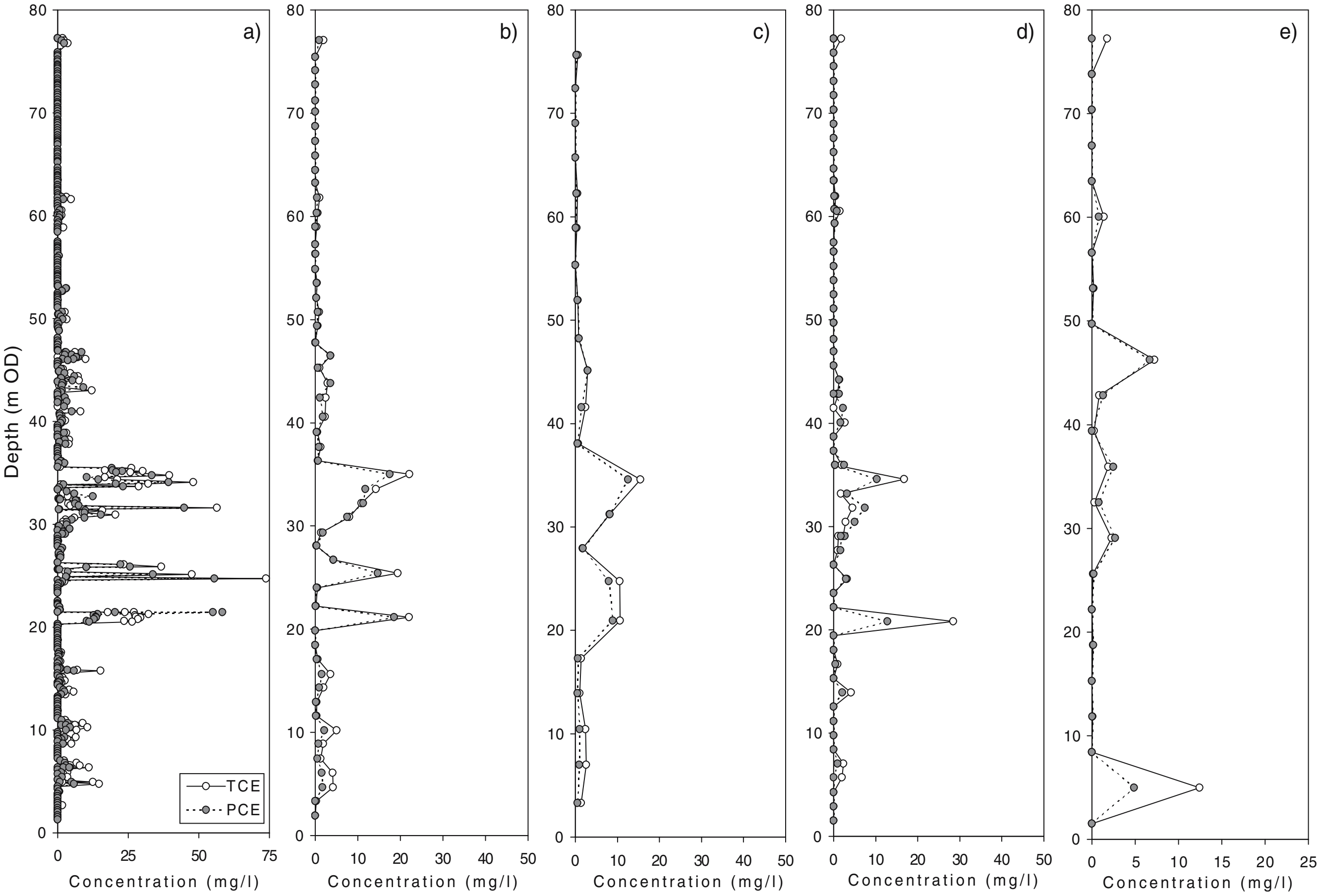

Fig. 9 Depth profiles of solvent concentrations for the inclined borehole at different sampling intervals (note different concentration scales). **a** All results, **b** results averaged over 2 m, **c** results averaged over 5 m, **d** spot results per 2 m and **e** spot results per 5 m

Spot samples

Samples were selected at 2-m intervals from the total data set. For convenience this was from even-numbered lengths along the core from the surface. The samples were chosen mechanistically in that no account was taken of any lithological variations. The results are plotted in Fig. 9d. The loss of resolution is immediately apparent; whilst the main zones are still identifiable, most of the small CHC peaks are not distinct. The coincidence of high CHC concentrations and the less permeable lithologies has disappeared and the maximum concentrations are significantly lower by a factor of two or three. Thus it would be difficult from this data alone to draw any conclusions on how these low-permeability layers control contaminant transport. When the frequency is reduced to 5-m intervals, even the main contaminated zones are 'lost', making any sensible interpretation impossible (Fig. 9e).

Implications

The implications of this are two-fold. Firstly that the sampling interval selected is crucial, especially where the data are required either to indicate the controls on contaminant movement or the maximum concentration in the subsurface. Secondly, where the number of analyses needs to be limited, the bulking of samples is to be preferred to collecting 'spot' samples. The sampling interval needs to be selected with regard to the scale over which significant changes occur in the hydraulic properties of the aquifer, since this is correlated to the presence/absence of CHCs. In this type of aquifer, this would relate to bed thickness which, at the case study site, is typically on the submetre scale. At this particular site, the fracture density did not appear to be a determining factor.

Conclusions

Following spillages of CHCs on a dual-porosity sandstone aquifer, significant quantities may be retained in the unsaturated zone. Drilling to obtain concentration profiles in the unsaturated zone is likely to be required to establish their phase and distribution. These data, together with other information, would provide the basis for a risk assessment and for any appropriate follow-up remediation or containment programme.

At the case study site, detailed sampling of CHCs in deep boreholes was able to provide invaluable information on both the extent and possible phase of contaminant migration. Where CHC concentrations are high, it may be difficult to distinguish whether migration occurred as the aqueous or NAPL phase. At this site, the consistent ratio of the two main CHC components of the plume provided strong evidence of movement in the aqueous phase and this was supported by the similar distribution of co-disposed aqueous phase inorganic components in the unsaturated zone.

The density or spacing of sampling is of crucial importance for understanding contaminant movement and should be on a similar scale to the heterogeneity which governs contaminant distribution. In the upper part of the Sherwood Sandstone aquifer of north-west England, where significant parts of the aquifer have jigsaw-type architecture, significant changes in lithological type and permeability occur over vertical distances of less than 1 m and samples need to be collected at this interval.

Where the sampling interval needs to be constrained, the bulking of samples over each sampled interval is more representative than taking spot samples and should be preferred. Bulking samples produces the anticipated loss of maximum concentration and resolution but retains a similar overall CHC distribution, whereas for spot samples, the relationship between high CHC concentrations and the less permeable lithologies may be lost.

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References

Abriola LM, Bradford SA (1998) Experimental investigations of the entrapment and persistence of organic liquid contaminants in the subsurface environment. Environ Health Perspect 106(Suppl 4): 1083–1095

Allen DJ, Brewerton LJ, Coleby LM, Gibbs BR, Lewis MA, MacDonald AM, Wagstaff SJ, Williams AT (1997) The physical properties of major aquifers in England and Wales. Tech Rep WD/97/34. British Geological Survey, Keyworth

Allen DJ, Bloomfield JP, Gibbs BR, Wagstaff SJ (1998) Fracturing and the hydrogeology of the Permo-Triassic sandstones in England and Wales. Tech Rep WD/98/1. British Geological Survey, Keyworth

Aurand K, Friesel P, Milde G, Neumayr V (1981) Behaviour of organic solvents in the environment. Stud Environ Sci 12: 481–487

Bloomfield JP, Gooddy DC, Bright MI, Williams PJ (2001) Pore-throat size distributions in Permo-Triassic-Triassic sandstones from the United Kingdom and some implications for contaminant hydrogeology. Hydrogeol J 9:219–230

Broholm K, Feenstra S (1995) Laboratory measurements of the aqueous solubility of mixtures of chlorinated solvents. Environ Sci Technol 14(1):9–15

Burston MW, Nazari MM, Bishop PK, Lerner DL (1993) Pollution of groundwater in the Coventry region (UK) by chlorinated hydrocarbon solvents. J Hydrol 149:137–161

Edmunds WM, Bath AH (1976) Centrifuge extraction and chemical analysis of interstitial waters. Environ Sci Technol 10:467–472

Edmunds WM, Cook JM, Kinniburgh DG, Miles DL, Trafford JM (1989) Trace element occurrence in British groundwaters. Res Rep SD/89/3, British Geological Survey, Keyworth

ENDS (2000) Village blighted by pollution from ICI Runcorn's old waste tips. ENDS Rep 301:4–5

Gooddy DC, Bloomfield JP, Harrold G, Leharne SA (2002) Towards a better understanding of tetrachloroethene entry pressure in the matrix of Permo-Triassic sandstones. J Contam Hydrol 59:247–265

Grabow GL, Mote CR, Sanders WL, Smoot JL, Yoder DC (1993) Groundwater monitoring network design using minimum well density. Water Sci Technol 28:327–335

Hooker PJ, Bridge DMcC, Brown MJ, Lawrence AR, Gooddy DC (1999) An integrated hydrogeological study of a post-industrial city in the West Midlands of England. In: Chilton PJ (ed) Groundwater in the urban environment: selected city profiles. Balkema, Rotterdam, pp 145–150

Horvath A (1982) Halogenated hydrocarbons: solubility/miscibility with water. Dekker, New York

Hull E (1982) Geology of the country around Prescot, Lancashire. Memoirs of the Geological Survey, England and Wales, old series county quarter sheet 80NW. British Geological Survey, Keyworth

Hunt J, Sitar N, Udell KS (1988) Nonaqueous phase liquid transport and clean up. 1. Analysis of mechanisms. Water Resour Res 24 (8):1247–1258

Keller AA, Blunt MJ, Roberts PV (2000) Behaviour of nonaqueous phase liquids in fractured porous media under two-phase flow conditions. Trans Porous Media 38:189–203

Keuper BH, Abbot W, Farquhar G (1989) Experimental observations of multiphase flow in heterogeneous porous media. J Contam Hydrol 5:83–95

Lawrence AR, Chilton PJ, Barron RJ, Thomas WM (1990) A method for determining volatile organic solvents in chalk porewaters (southern and eastern England) and its relevance to the evaluation of groundwater contamination. J Contam Hydrol 6:377–386

Lawrence AR, Barker JA, Bird MJ, Gooddy DC, Marks RJ, Stuart ME (1992) Review of groundwater pollution of the Triassic sandstone aquifer by the halogenated solvents. R&D Note 47, National Rivers Authority, Bristol

Mackay DM, Cherry JA (1989) Groundwater contamination: pump and treat remediation. Environ Sci Technol 23(6):630–636

Maidwell FT (1914) Some sections in the Lower Keuper of Runcorn Hill, Cheshire. Trans Liverpool Geol Assoc 12:40–52

Maidwell FT (1915) Some sections in the Lower Keuper of Runcorn Hill, Cheshire II. Trans Liverpool Geol Assoc 12:141–149

Mercer JW, Cohen M (1990) A review of immiscible fluids in the subsurface: properties, models, characterization and remediation. J Contam Hydrol 6:107–163

Moran MJ, Davis AD (1998) Occurrence of selected volatile organic compounds in groundwater of the United States, 1985–1995: relations with hydrogeologic and anthropogenic variables. Proc. of 18th Annual American Geophysical Union Hydrology Days, Fort Collins, CO, 30 March–3 April 1998, pp 201–211

NRC (1994) Alternatives for ground water clean-up. National Academy Press, Washington, DC

Parker BL, Gillham RW, Cherry J (1994) Diffusive disappearance of immiscible-phase organic liquids in fractured geologic media. Ground Water 32(5):805–820

Poulsen MM, Keuper BH (1992) A field experiment to study the behaviour of tetrachloro-ethylene in unsaturated porous media. Environ Sci Technol 26(5):889–895

Price M (1977) Specific yield determinations from a consolidated sandstone aquifer. J Hydrol 33(1–2):147–156

Price M (2003) The origin and extent of some fissures in sandstones. In: Krasny J, Bruthans J (eds) Groundwater in fractured rocks. IAH, Prague, Czech Republic

Price M, Morris BL, Robertson A (1982) A study of permeability variations in Chalk and Permian aquifers, using double packer injection testing. J Hydrol 54:401–423

Reynolds DA, Kueper BH (2004) Multiphase flow and transport through fractured heterogeneous porous media. J Contam Hydrol 71:89–110

Rivett MO, Lerner DN, Lloyd JW (1990a) Chlorinated solvents in UK aquifers. J Inst Water Environ Manage 4:242–250

Rivett MO, Lerner DN, Lloyd JW, Clark L (1990b) Organic contamination of the Birmingham aquifer, UK. J Hydrol 113: 307–323

Sterling SN, Parker BL, Cherry JA, Williams JH, Lane JW Jr, Haeni FP (2005) Vertical cross-contamination of trichloroethylene in a borehole in fractured sandstone. Ground Water 43 (4):557–573

Stuart ME (1991) Determination of chlorinated solvents in aquifer porewaters. Tech Rep WD/91/37, British Geological Survey, Keyworth

Sudicky EA, Slough KJ, Forsyth PA (1998) DNAPL migration in fractured porous rock media: parameter sensitivity, prediction uncertainty and implications for remediation. Groundwater quality, Remediation and Protection (Proceedings of the GQ'98 Conference held as Tubingen, Germany, 1998) IAHS Publ. no. 250, IAHS, Wallingford, UK

Tait NG, Lerner DN, Smith JWN, Leharne SA (2004) Prioritisation of abstraction boreholes at risk from chlorinated solvent contamination on the UK Permo-Triassic Sandstone aquifer using a GIS. Sci Total Environ 319:77–98

Toussaint BB, Weyer KU (1992a) Limitations of sampling subsurface contamination by volatile hydrocarbons in unconsolidated, fractured and karstic rocks. 1. Practical experiences from 220 cases. In: Weyer KU (ed) Subsurface contamination by immiscible fluids. Balkema, Rotterdam, pp 277–286

Toussaint BB, Weyer KU (1992b) Limitations of sampling subsurface contamination by volatile hydrocarbons in unconsolidated, fractured and karstic rocks. 2. Evaluation of three case histories. In: Weyer KU (ed) Subsurface contamination by immiscible fluids, Balkema, Rotterdam, pp 287–295

Vucetic S, Obradovic Z (2000) Examination of the influence of data aggregation and sampling density on spatial estimation. Water Resour Res 36:3721–3730

Walker RG, Cant DG (1984) Sandy fluvial systems. In: Walker RG (ed) Facies models, 2nd edn., Geoscience Canada, St. John's, NL, Reprint Ser 1:71–89

Walthall S, Ingram JA (1981) Further work on the hydraulic properties of the sandstone aquifer at Padgate, Warrington. Hydrogeological Report 78, North West Water Authority, Warrington, UK

Walthall S, Campbell JE (1986) The measurement and interpretation of permeability values with special reference to fissured aquifers. Special Publication of the Geological Society Engineering Group No. 3, Geological Society Engineering Group, London, pp 273–278

Wealthall GP, Steele A, Bloomfield JP, Moss RH, Lerner DN (2001) Sediment filled fractures in the Permo-Triassic sandstones of the Cheshire Basin: observations and implications for pollutant transport. J Contam Hydrol 50:41–51

WHO (1998) Guidelines for Drinking Water Quality. World Health Organisation, Geneva

Wray DA (1937) BGS Fieldslip No. FS/3247; County Sheet Cheshire 24NE (W). Fieldslip with sectional descriptions from the Beacon Hill and Weston quarries. British Geological Survey, Keyworth