

Investigating the scale of structural controls on CHC 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 the Triassic Sherwood Sandstones of the UK, a fractured porous aquifer, is discussed and the requirements for successful investigation methodologies are considered. The study site was on gently dipping sandstones adjacent to a linear lagoon historically used to dispose of industrial wastes containing chlorinated solvents. Two sandstone cores of more than 100 metres length were recovered and measurements of chlorinated hydrocarbons (CHCs), inorganic chemistry, lithology, fracturing and aquifer properties were made. The results were used to 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 in an aquifer. 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 one metre 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 as a non-aqueous phase. (224 words)

Keywords

Chlorinated solvents, Sampling, Fractured media, Permo-Triassic Sandstone, 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 (Aurang 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, 1992b; 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 manufacture 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. 2003).

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.

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 fluvial 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. 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.

The upper part of the Sherwood Sandstone consists of mainly jigsaw architecture. In the Helsby Sandstone (Table 1), sheet and lenticular channel sandbodies 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.....more editing needed.

Aquifer transmissivities for the sandstones range from 1 to 5000 m²/d (median 189 m²/d) and well yields of 5,000 m³/d 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/d 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 airfilled) 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 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 regional flow it is flow through the matrix 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 regional flow 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 Permian-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 (Goody 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 sub-vertical 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 sub-vertical fractures are thought to be sediment filled which considerably reduces the permeability contrast with the matrix;
- many vertical or sub-vertical 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' (remove Fig. 3). 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 Keuper, 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 PCE, 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. This plume will itself be attenuated by diffusion into the matrix. Back diffusion from the rock to the fractures may occur over a very long period of time (Lipson et al, 2005). 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 (1882), Mainswell (1914 and 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 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 metres, 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 minimise the contamination of porewater by drilling fluid

and to prevent the mobilisation of DNAPL, should a 'pool' be penetrated (Sterling et al. 2005). Large amounts of mud were required where major vertical fractures were intersected by the inclined hole??. The extent of invasion of the core by drilling 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 added and the vial sealed directly (Stuart 1991). Expected variations in aquifer properties on the sub-metre 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 2 to 4 metres 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.

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 high contaminant concentrations in the porewaters appear to correspond with parts of the aquifer where mudstone layers were delineated by core and geophysical borehole logging, perhaps indicating a degree of ponding on and diffusion into mudstone horizons (e.g. at 28, 21, 7.1 and -2 m OD). The differing sampling interval and methodologies used for the various parameters makes a statistical analysis difficult.

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 movement 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 *pers com*), 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 $1.11 \times$ 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.

Fig. 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 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 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 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 metres. 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 metre intervals;
- Bulked samples at 5 metre intervals.

- Spot samples (i.e. from discrete 1-cm depth range) at 2 metre intervals;
- Spot samples at 5 metre 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 metre intervals this represented usually six subsamples. The results are plotted for 2 and 5 metre intervals in Fig. 9b and 9c. It can be seen from Fig. 9b that when samples are bulked over 2-metre 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 metres the resolution is diminished further but the main zones can still be identified.

Spot Samples

Samples were selected at 2-metre 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-metre 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 sub-metre 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 one metre and samples need to be collected at this interval. At frequencies of 2 metres or more considerable resolution and peak concentrations are reduced or not observed, and the relationship with aquifer structure is unclear.

The bulking of samples over the sampled interval is more representative than spot samples and should be preferred.

Acknowledgements

The authors are grateful to their many colleagues in BGS and ICI who have contributed to the work described here. This paper is published by permission of the Executive Director of the British Geological Survey (NERC).

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

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

Table 2 Summary of fracture characteristics for the Sherwood Sandstones of the Runcorn peninsula (from Bloomfield unpublished report and Wealthall et al. 2001)

Fracture orientation	Type	Spacing (m)	Aperture (mm)	Length (m)
NNW-SSE	Dominant sub-vertical multilayer cross-cutting outcrop	10 – 20	0.2 – 27	>5
NNW-SSE	Minor, sub-vertical	2.5	<1	<2
WSW-ENE	Minor, sub-vertical	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

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

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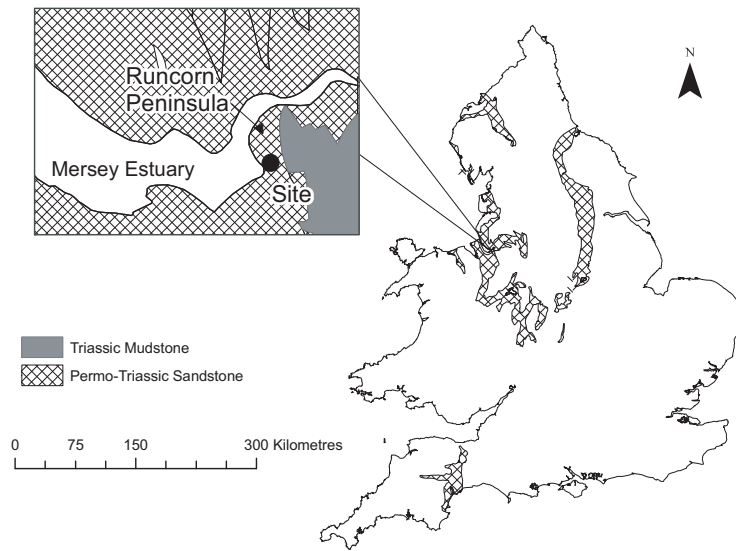
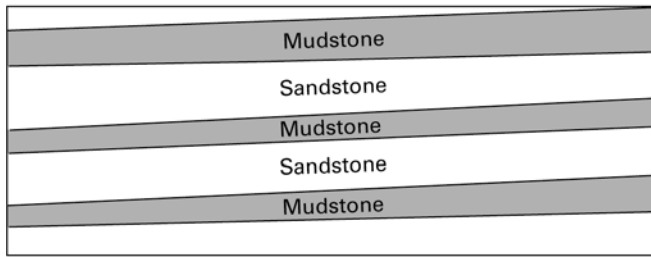


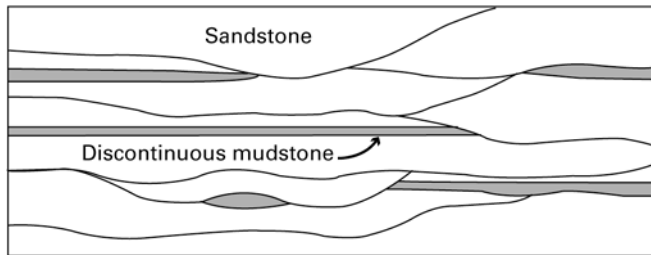
Fig 1

LAYER-CAKE



Distinct layering with marked continuity and gradual thickness changes. Mudstones act as barriers

JIGSAW



Different sandstone bodies fit together without major gaps. Occasionally low-permeability mudstones act as local baffles but not complete barriers

Fig. 2

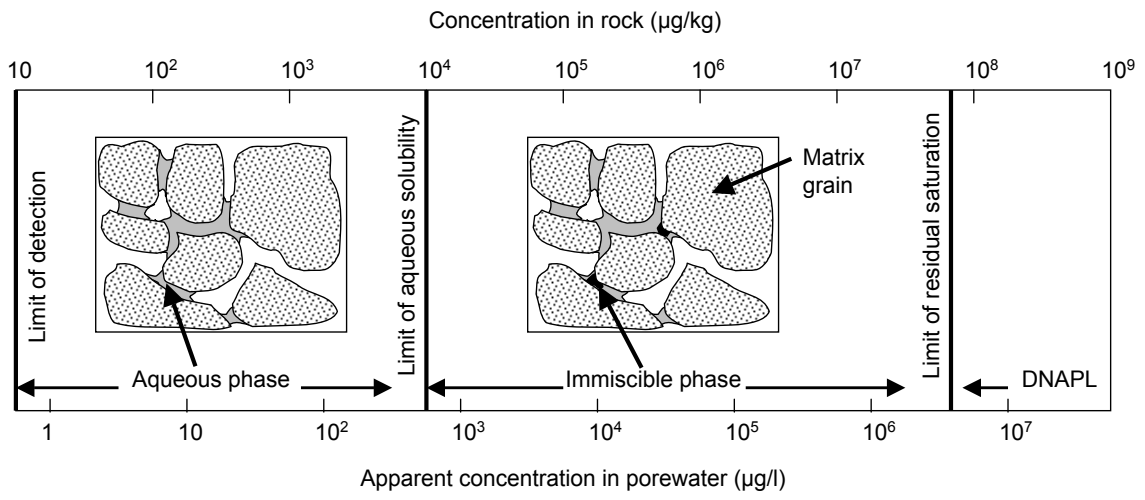


Fig 3

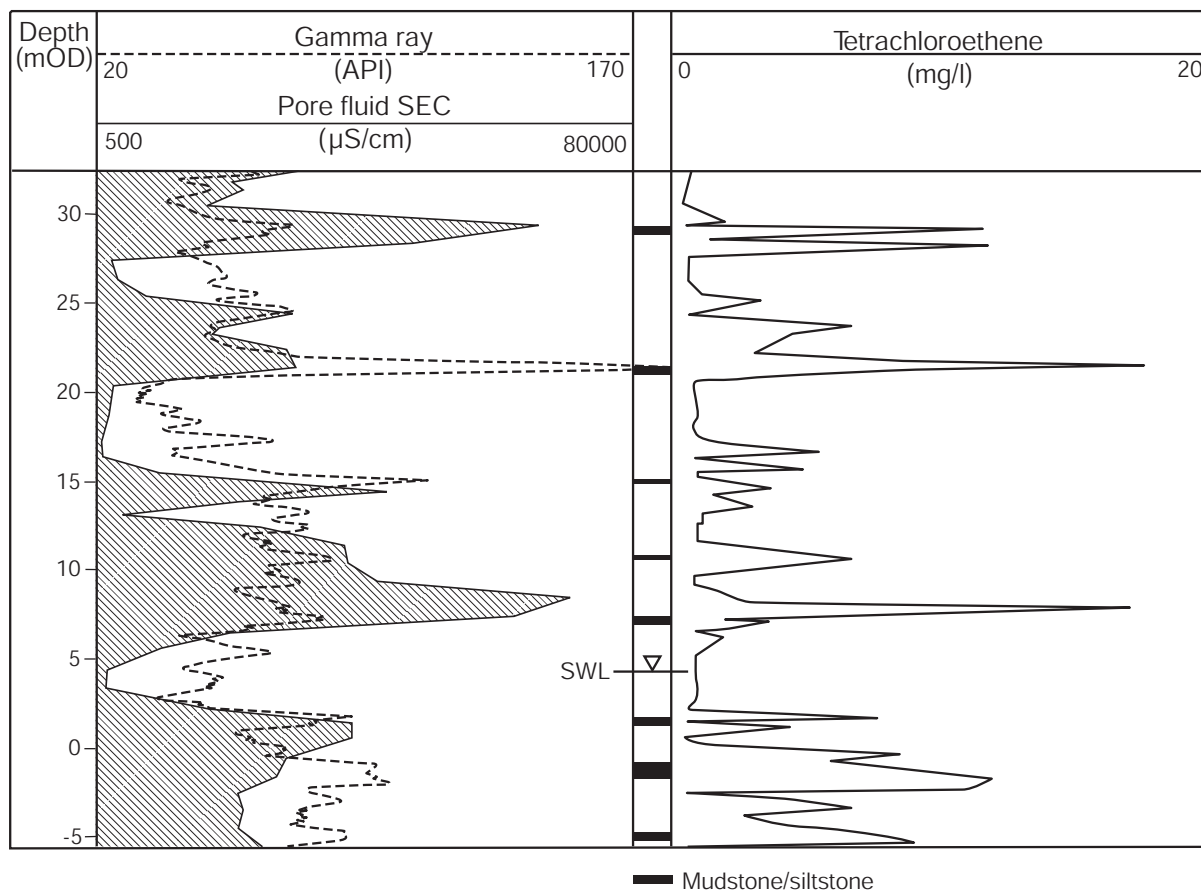
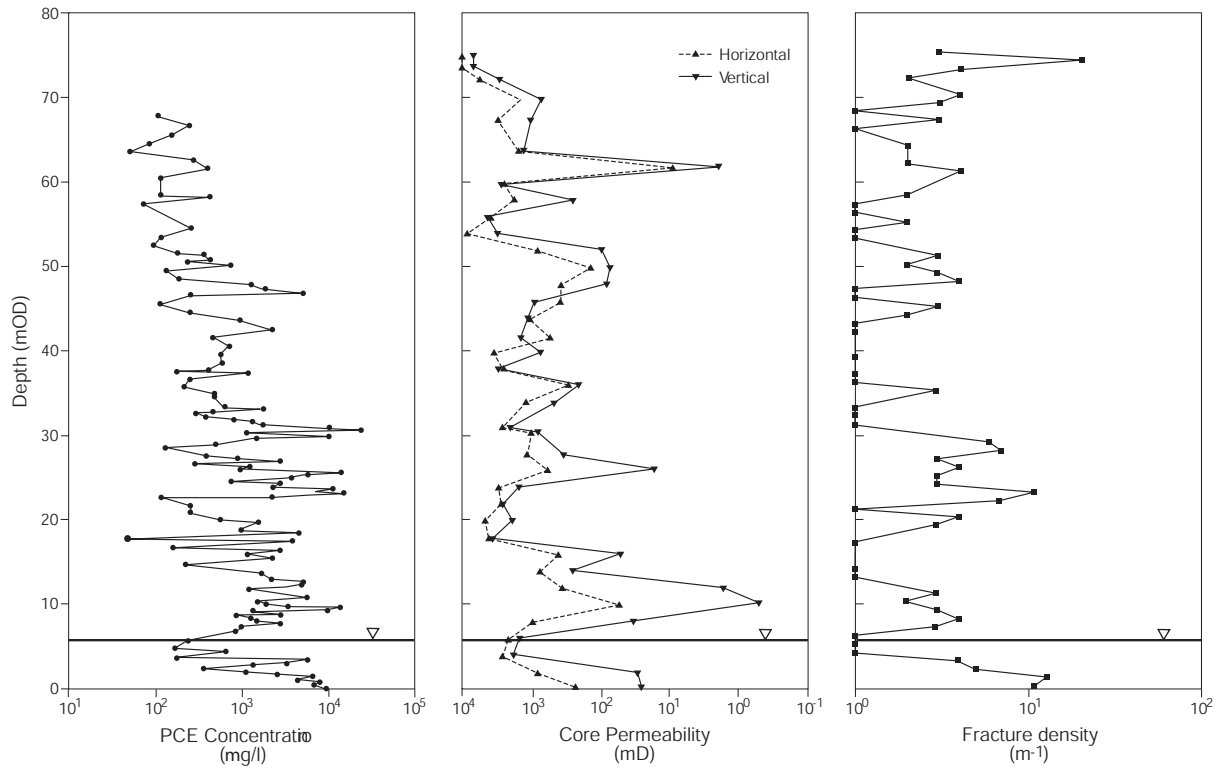


Fig 4



The milliDarcy (mD) is the most commonly used unit of intrinsic rock permeability, approximately equivalent to $10^{-3} \mu\text{m}^2$

Fig 5

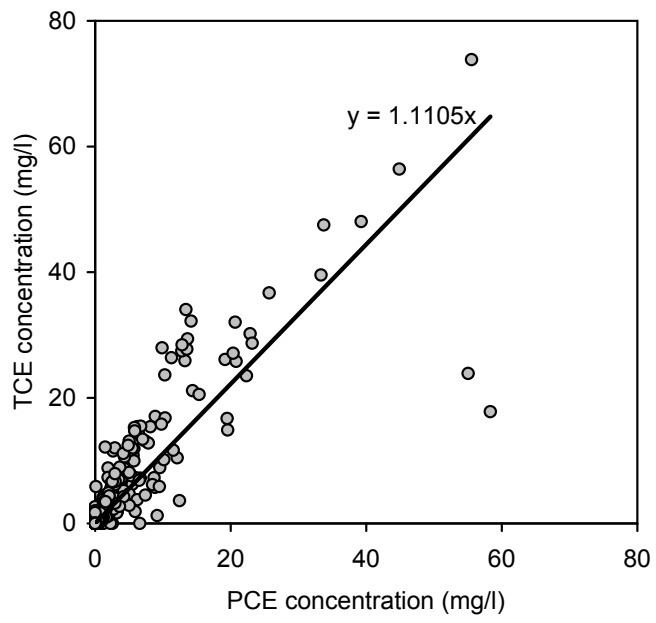


Fig 6

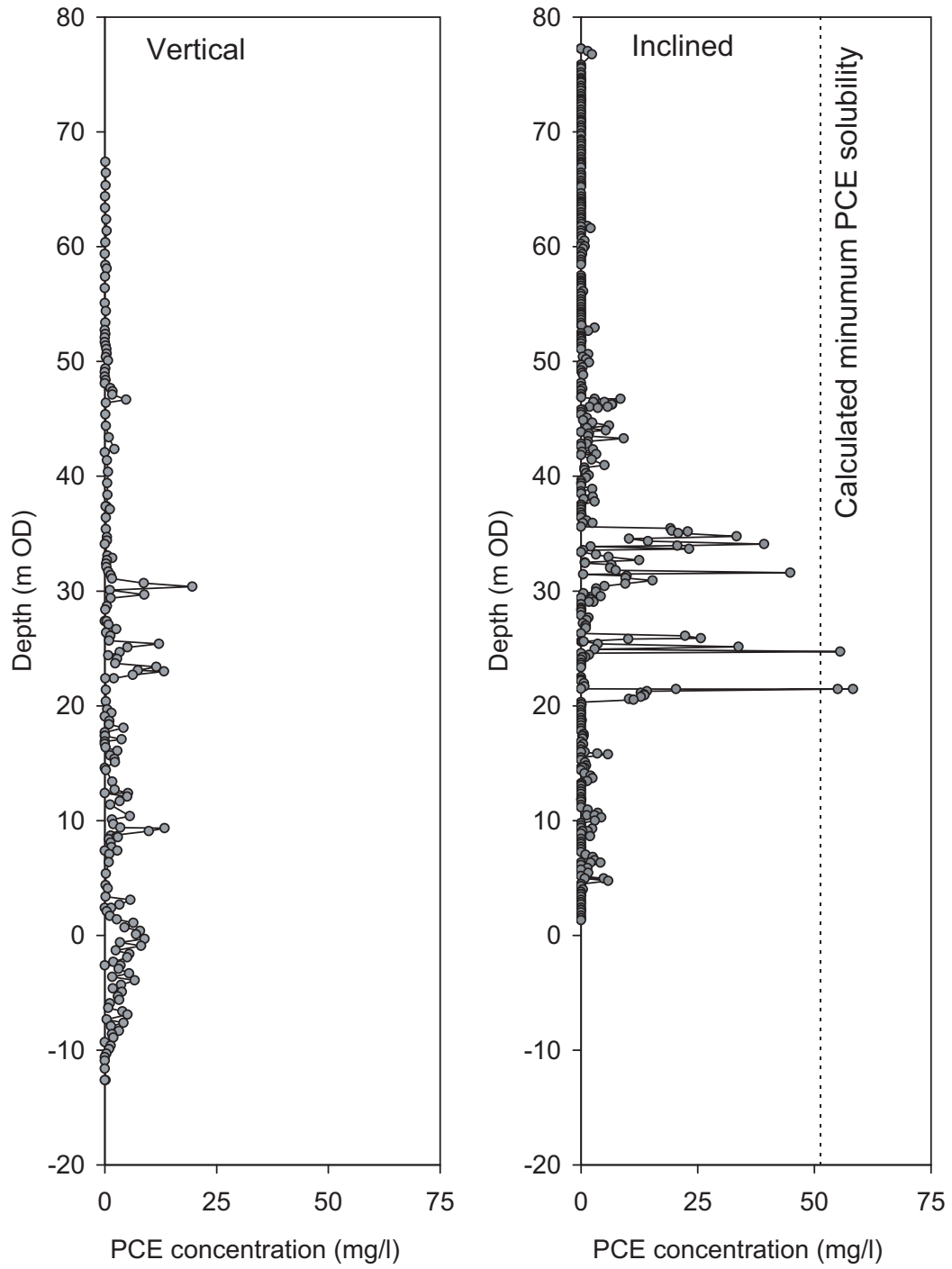


Fig 7

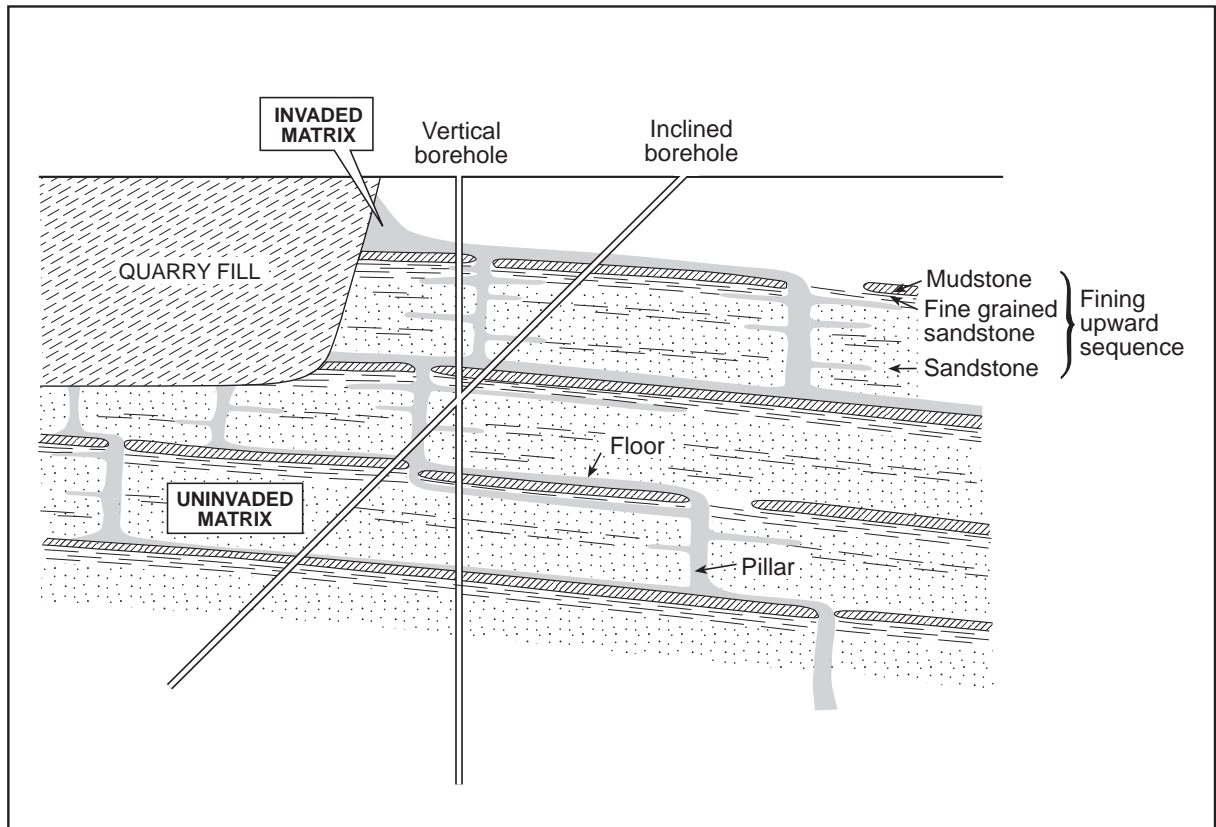


Fig 8

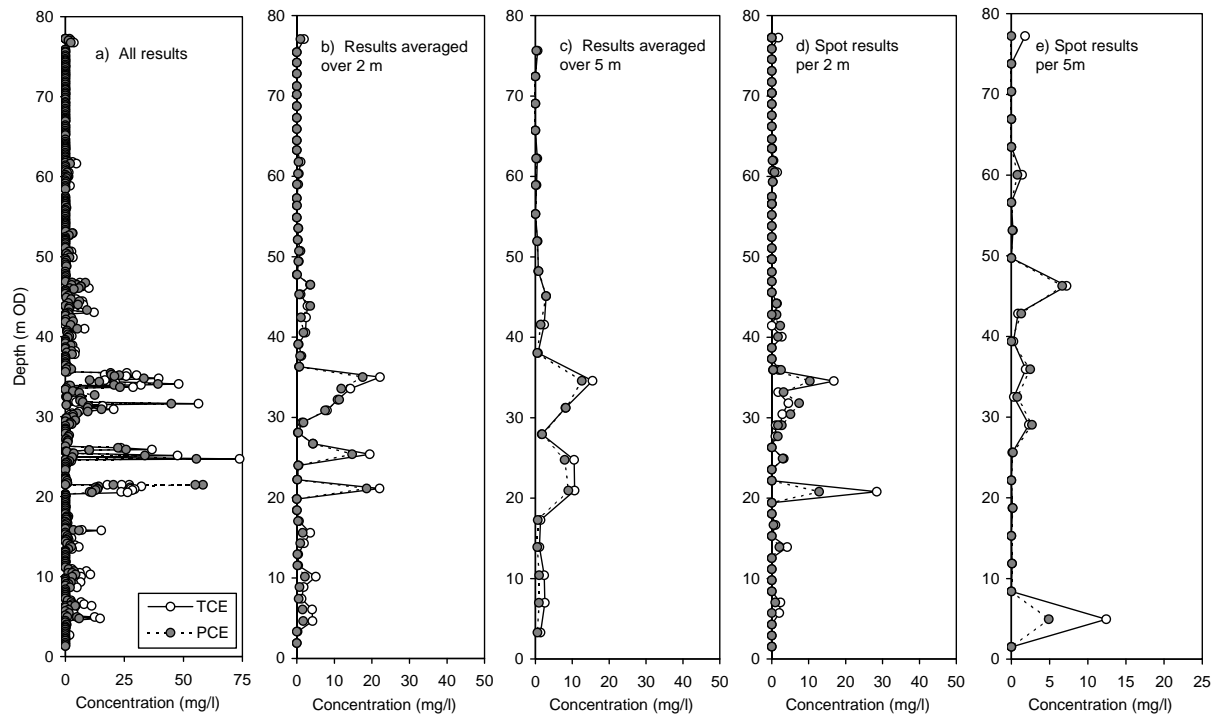


Fig 9