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# Challenges in monitoring the natural attenuation of spatially variable plumes

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## Abstract

Monitored natural attenuation may be applied as a risk-based remediation strategy if it can be established that contaminants are or will be reduced to some acceptable level at or before a compliance point. Contaminant attenuation is often attributed to intrinsic biodegradation, which in some circumstances may occur only at the plume fringes where electron acceptors from the surrounding uncontaminated zones mix by dispersion and diffusion with the plume. However, due to the common spatial and temporal variability exhibited by many plumes, the centreline monitoring approaches advocated in many natural attenuation protocols may be unable to detect natural attenuation occurring primarily by fringe processes. Snapshot data from a multilevel sampling well transect across an MTBE plume at Vandenberg Air Force Base, CA, USA, illustrate the difficulty of centreline monitoring and the challenge of providing sufficient detail to detect attenuation processes that may be occurring primarily at plume fringes. In a study of a phenols plume in Wolverhampton, UK, high-resolution multilevel wells demonstrated that the key biodegradation processes were restricted spatially to the upper fringe of the plume and were rate-limited by transverse dispersion and diffusion of electron acceptors into the plume. Thus the overall extent of biodegradation was considerably less than suggested by a plume-scale analysis of total electron acceptor and contaminant budgets. These examples indicate that more robust and cost-effective MNA assessments can be obtained using monitoring strategies that focus on the location of key biodegradation processes.

## Introduction

Monitored natural attenuation (MNA) has rapidly become an acceptable tool for the risk-based management of some types of groundwater contaminant plumes, especially petroleum hydrocarbons and their derivatives (McAllister & Chiang 1994; Kampbell et al. 1996; Wiedemeier et al. 1996; Kao & Wang 2000; Kao & Prosser 2001; Suarez & Rifai 2002). Natural attenuation (NA) processes comprise sorption, dispersion, volatilisation, dilution, abiotic degradation and biodegradation, but only degradation processes result in the transformation of contaminants, ideally to non-toxic by-products. Often, it is only the biologically mediated degradation processes (biodegradation) that are significant in mass reduction. Thus, the numerous and often lengthy technical guidance protocols for the assessment of MNA focus predominantly on gathering geochemical evidence to support or reject the hypothesis that biodegradation is occurring at a rate that is sufficiently protective of risk (Wiedemeier et al. 1995). These protocols generally advocate the collection of data to build multiple lines of evidence, usually from monitoring wells installed along what is presumed to be the plume centreline. The primary line of evidence is obtained by using contaminant concentration data to infer mass loss via degradation (e.g. from analysis of concentration versus distance at several times) and to assess whether the plume is expanding, at steady state or shrinking. Secondary evidence includes data on the distribution of reaction products and redox-sensitive species to demonstrate the "footprint" or geochemical signature of degradation processes in the plume. Tertiary evidence includes direct indication that microbes capable of the desired reaction are active at the site. This latter evidence has traditionally been established via microcosm studies, but recently developed techniques in molecular microbiology have made it possible to screen sites for specific genetic markers and other key indicators.

In the early phase of site investigations, consultants and regulators often seek to define contaminant distributions using as few long-screened wells as possible. Unfortunately, such monitoring networks are often too sparse to be of much use in an NA assessment, which means that additional wells must be installed for that purpose. A confounding problem in the design of monitoring well networks for NA assessments is that the distribution of contaminants and the development of the plume are significantly influenced by spatial and temporal heterogeneity in aquifer properties and local hydrological conditions. We now explore the importance of these factors by considering a series of generic plume scenarios (not exhaustive of all possible scenarios) based on some of the factors that give rise to spatially and temporally variable contaminant distributions. If the goal is to install a series of wells along the plume centreline, it is necessary to determine if the plume geometry is simple enough so that the plume possesses a unique or representative centreline that can be identified and instrumented. In the case where this reflects real conditions, as illustrated in Figure 1a, then centreline monitoring may be adequate and methods such as those described by Buscheck & Alcantar (1995) may be used to estimate a pseudo-first order contaminant attenuation rate. Note that, while a plume may indeed have a single dominant migration path (i.e. a centreline) it may be missed by monitoring wells installed based on assumed, but incorrect, groundwater flow directions (Figure 1b). Furthermore, macro-scale geological heterogeneity (buried stream channels, etc) may result in a "centreline" that may wander in all three dimensions (plan view only shown in Figure 1c).

It is also possible that the contamination migrating from a source area may not have a unique centreline, but may instead consist of a number of relatively discrete plumes of varying flux (strength and/or rate of migration), which reflect preferred migration pathways (Figure 1d) and/or heterogeneously distributed sources (Figure 1e). Preferred flux paths develop because aquifers are seldom homogenous in terms of the physical and chemical properties that control contaminant distribution and transport (Cozzarelli et al. 1999). Depositional environments are inherently heterogeneous in their structure, and complex stratigraphy (cross bedding, interbedding, discontinuities, etc) can be expected to result in spatially variable distributions of hydraulic conductivity and preferred flow paths (Jankowski et al. 1997; Lee et al. 2001). Contaminant flux from source zones may also vary temporally as a result of source term evolution, water table fluctuations and changes in groundwater flow direction (McMahon & Bruce 1997; Davis et al. 1999; McGuire et al. 2000). Such variability may occur on the scale of weeks to months (water table and flow direction changes) or years (source term aging and compositional changes). Therefore, either more detailed site characterisation than is typically applied at many sites may be needed to allow accurate placing of centreline wells or centreline monitoring should be ruled out altogether. Where spatial or temporal heterogeneity precludes centreline monitoring, an alternative monitoring strategy is needed.

It would seem obvious that, in the case of attenuation by intrinsic biodegradation, the appropriate monitoring approach would be one that focuses on the zones within the plume where dominant biodegradation reactions occur. In general, effective NA is a dynamic balance between electron donors (both target and non-target species) and dissolved and mineral electron acceptors. However, the majority of contaminant turnover may be constrained to discrete areas of a plume because degradation is limited to certain redox conditions or organisms and/or there may be deficiencies in the supply of background electron acceptors or other required species (Lyngkilde & Christensen 1992; Rügge et al. 1995; Davis et al. 1999; Cozzarelli et al. 2001). One common conceptual model suggests that the microbial consortia that biodegrade, for example, fuel hydrocarbons, PAHs and phenols, consume electron acceptors in the order $O_2$, $NO_3^-$, $MnO_2$, $Fe(OH)_3$, $SO_4^{2-}$, $CO_2$. This may result in the development of sequential electron acceptor-depleted methanogenic redox conditions in the plume core grading to aerobic conditions at the fringe (Champs et al. 1979; Barcelona et al. 1989; Smith 1997; Chapelle et al. 2002). Recently, however, field studies have shown that the attenuation of, for example, phenolics (Thornton et al. 2001) and fuel oxygenates (Landmeyer et al. 2001) is dominated by aerobic and $NO_3^-$-reducing biodegradation confined to the plume fringes. Weak vertical dispersive mixing means that these fringes may be less than 1 m thick (Davis et al. 1999; Schreiber & Bahr 1999; Cozzarelli et al. 1999; Cozzarelli et al.

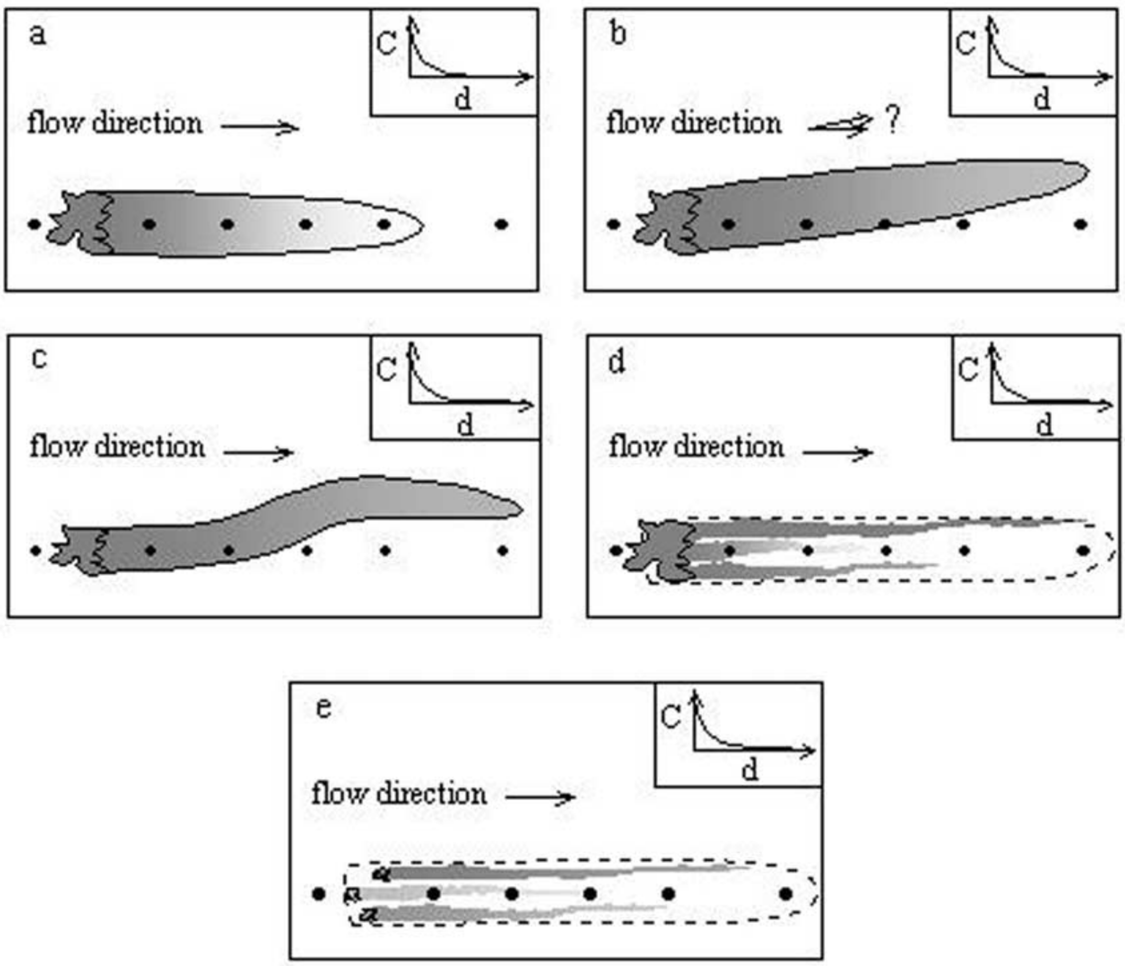

*Figure 1.* Conceptual diagrams illustrating difficulty in establishing and instrumenting representative centreline monitoring in different scenarios: (a) uniformly distributed plume in homogeneous, isotropic media, (b) uniformly distributed plume in homogeneous, isotropic media where hydraulic gradient is inaccurately defined, (c) uniformly distributed plume in media with undetected macro-scale heterogeneity (i.e. buried stream channel), (d) non-uniformly distributed plume migrating along preferred flux paths in heterogeneous media, (e) non-uniformly distributed plume generated from heterogeneously distributed sources. Dots represent monitoring wells and insets show resulting concentration vs distance along instrumented transect.

2001; McGuire et al. 2000) and exhibit steep chemical gradients of both electron acceptors and donors. Conversely, some organisms can use halogenated solvents as terminal electron acceptors during reductive dehalogenation (Holliger & Schumacher 1994). This requires the presence of hydrogen (electron donor) and strongly anaerobic conditions that are typically found only near the core of such plumes.

Thus, the challenge of NA assessment monitoring is to adequately resolve these discrete terminal electron acceptor process (TEAP) zones, since the information gained provides the chemical framework to quantify attenuation processes and therefore predict the bioattenuation potential of the plume as a whole. However, long-screened monitoring wells may straddle multiple TEAP zones, destroying any gradients and diluting or averaging concentrations of dissolved organics, electron acceptors and redox indicators. This sampling artefact has been shown to result in the erroneous interpretation of dominant TEAPs in plumes and up to 75% underestimation of assimilative capacity (Martin-Hayden & Robbins 1997; Schreiber & Bahr 1999). Accurate delineation of TEAP zones in plumes, in support of an NA assessment, therefore requires a re-appraisal of traditional monitoring

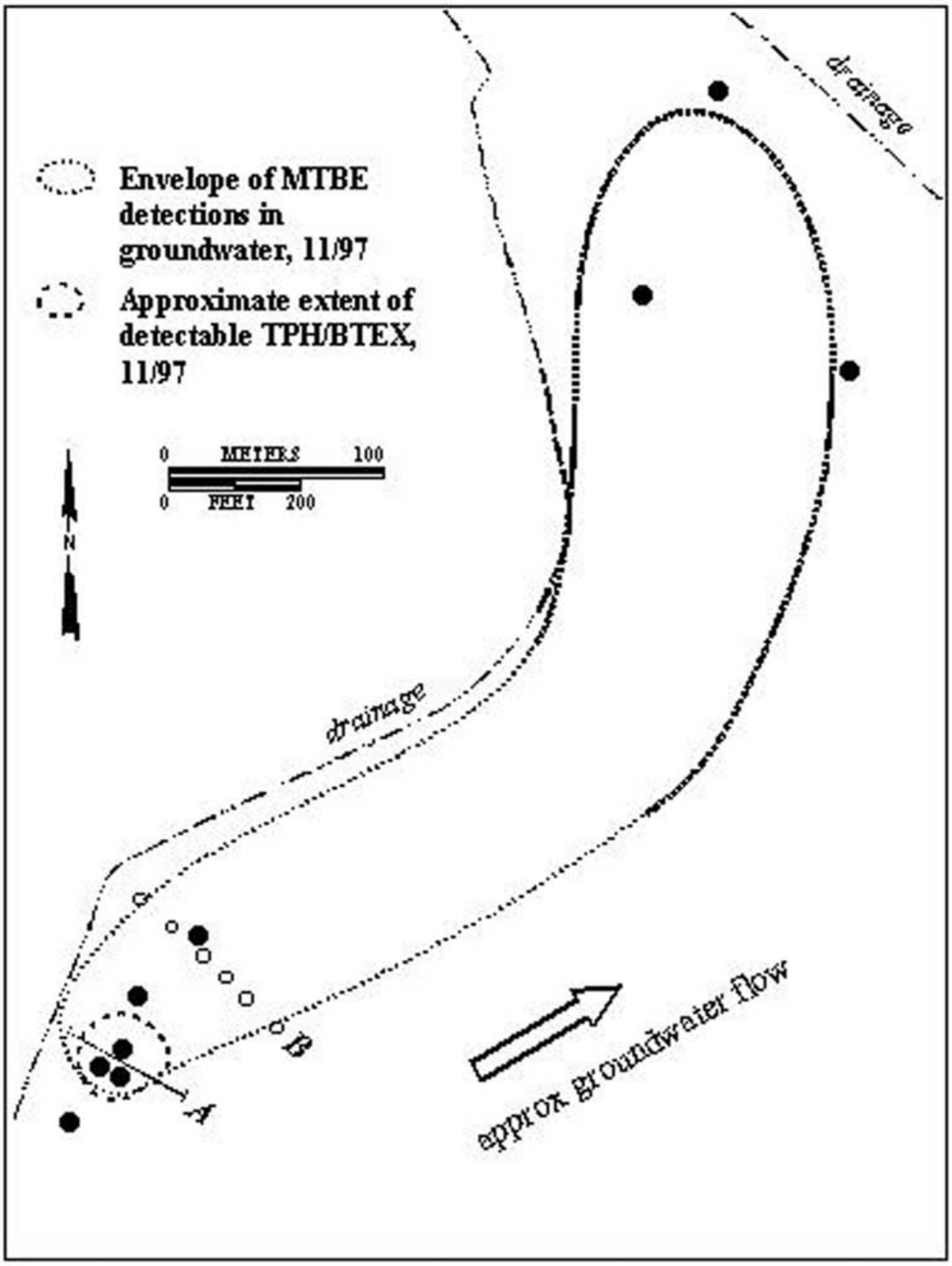

*Figure 2.* Map of VAFB MTBE plume showing location of consultant monitoring wells (solid dots) and multilevel wells (open dots) along Transect B.

approaches to account for the inherent heterogeneity in the distribution of such processes.

It has recently been proposed that mass flux estimation may be a more practical method to assess natural attenuation (Bockelmann et al. 2000, 2001). In principle, the total mass flux (mass discharge) of contaminants (or electron acceptors) across a hypothetical plane oriented transverse to the plume axis may be estimated by integrating spatial information on dissolved concentrations obtained from groundwater sampling with information on variations in total groundwater discharge across the plane. Multilevel monitoring well transects (Borden et al. 1997; Kao & Wang 2000; Einarson & Mackay 2001; Kao & Prosser 2001; Suarez & Rifai 2002) and integral pumping (Bockelmann et al. 2000, 2001) are two methods recently proposed to obtain total mass flux estimates. Comparing total mass flux estimates across different transects may reveal trends in attenuation that may not be apparent from, or may be misrepresented by, centreline concentration data, especially in the case of spatially variable plumes. However, if the key reactions occur only in the fringe areas of the plumes, both approaches may have difficulties detecting them: multilevel transects may not provide sufficiently detailed information across the reaction zones while pumping strategies may not pump long enough to draw water from the fringe zones into the extraction wells. In the following sections, we illustrate some of these points to highlight the need for a re-evaluation of current NA monitoring strategies.

## NA monitoring using multilevel transects

A methyl *tert*-butyl ether (MTBE) plume at Site 60, Vandenberg Air Force Base, California, has been studied since 1998 (Mackay et al. 2001; Wilson et al. 2002). The plume was originally characterised by consultants to the US Air Force by using a very sparse network of long-screened monitoring wells (e.g. one to several meters in length). The envelope of all detections of dissolved MTBE was determined to have the relatively simple shape shown in Figure 2; the bend in the plume apparently following diverging groundwater flow as the valley widens (Lee&Ro 1998).

Six Continuous Multi-Channel (CMT) multilevel wells (Einarson & Cherry 2002), a new type of permanent multilevel sampling device, were installed in a transect across the plume approximately 60 m downgradient of the source area (Transect B in Figure 2) early in the study, to characterise the plume with greater spatial resolution. These wells, each completed with 7 monitoring ports, were spaced between 6.1 and 12.2 m apart along Transect B (Figure 2). All the monitoring ports were developed by repeated surging and purging, and were then sampled using a peristaltic pump. Samples were collected and analysed for dissolved oxygen (DO), Eh and MTBE using methods previously described by Wilson et al. (2002). Eleven snapshots of Transect B were collected between March 1999 and October 2002; results of the first 6 snapshots are depicted in Figure 3. What is immediately apparent is that the plume has a complex and varying internal structure that could not have been identified via the long screen monitoring wells. The plume is composed of a series of high flux paths surrounded by more diffuse contamination, and these high flux paths apparently vary in strength and location through time. Temporal variability may be due to hydraulic factors in the source area (e.g. recharge variations), but it is nevertheless evident that this plume does not have a temporally stable centreline. This means that centreline monitoring is unlikely to be useful for assessing NA of MTBE at this site. High concentrations of $SO_4^{2-}$ exist throughout the plume (data not shown), indicating that methanogenesis is confined to the source area where petroleum hydrocarbons persist. Thus NA of MTBE at this site would have to occur under either less reduced anaerobic TEAPs or under aerobic conditions.

Prior work at the site based on artificial oxygen addition suggests that in situ aerobic bioremediation is possible and indeed quite rapid (Wilson et al. 2002), while the literature suggests that MTBE biodegradation under $NO_3^-$-, $Fe^{3+}$- or $SO_4^{2-}$-reducing conditions is likely to be much slower if it occurs at all (Suflita & Mormile 1993; Yeh & Novak 1994; Salanitro et al. 2000). Furthermore, the background groundwater is naturally anaerobic at the site, so intrinsic aerobic biodegradation will be limited to the upper plume fringe where mixing of infiltrating precipitation or oxygen diffusing into the water table from the vadose zone can occur. Since the contaminated permeable zone is only about 1.5 m thick and under semi-confined conditions most if not all of the year, despite significant seasonal fluctuations of water level, it would be very difficult to instrument the site with sufficient detail to detect any reactive fringe in the upper portion of the plume. Indeed, the fringe may exist within low permeability media, from which water samples cannot be easily drawn. For these reasons, it may also be true that over-

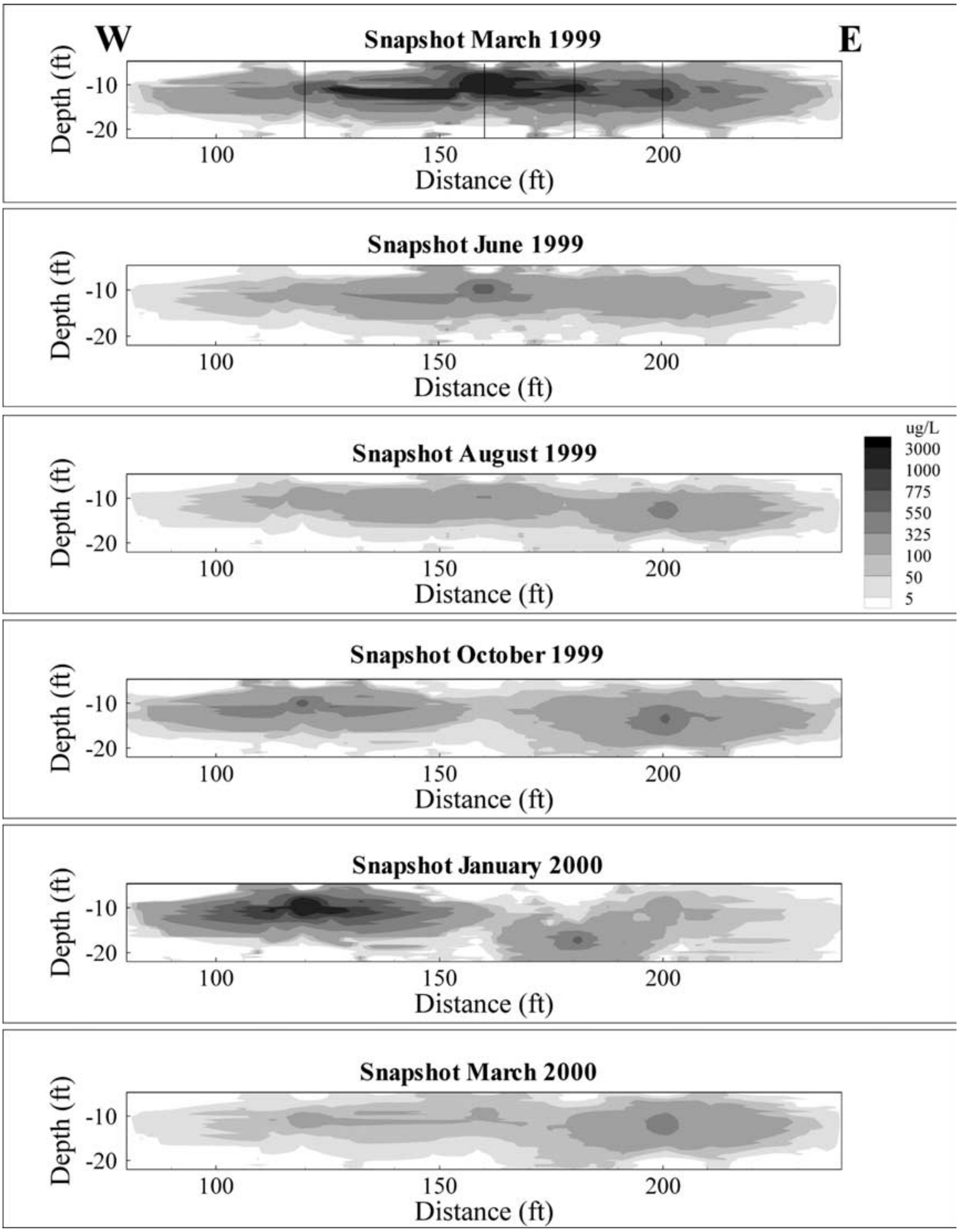

*Figure 3.* Snapshots of MTBE concentrations across Transect B at six times between March 1999 and March 2000. Marked spatial and temporal plume variability is evident. The West and East boundaries and the four black vertical lines in the top frame indicate the location of the 6 multilevel wells.

all the aerobic NA of the MTBE is limited at this site. If so, it can be anticipated that NA would be difficult to evaluate even with the approach based on estimates of MTBE mass discharge, since the methods would have to be quite precise in order to confidently identify small changes and differentiate them from variations that may arise from other factors (variations in source emanation rate, etc.). Nevertheless, work is continuing at VAFB to compare the apparent accuracy and precision of different mass discharge estimation methods. This work will be reported in future publications.

## Monitoring spatially variable biodegradation processes

Given the difficulties in determining degradation rates from either centreline or transect monitoring, identifying the types and spatial distribution of processes involved in contaminant degradation is an alternative approach to assessing natural attenuation. In general, the reduction in total organic carbon mass (target contaminants and non-target organics) via biodegradation should be balanced by an equivalent consumption of electron acceptors (in the absence of other demands for electron acceptors). As previously mentioned, TEAPs are generally spatially distributed with methanogenic conditions grading to aerobic activity outwards from the plume axis and source area. Various methods (Kampbell et al. 1996; McMahon & Bruce 1997; Wiedemeier et al. 1999; Lee et al. 2001; Thornton et al. 2001a; Suarez & Rifai 2002) have been proposed to incorporate spatially distributed TEAPs into an overall NA assessment, but most make simplifying assumptions regarding plume spatial uniformity. The accurate determination of the contribution of each of the TEAPs to the overall aquifer attenuation capacity for a given contaminant is therefore predicated on characterising the spatial distribution and concentration of all relevant electron donor and electron acceptor species. This is demonstrated by considering the following example of a complex plume of phenolic contaminants in a sandstone aquifer in the UK West Midlands (Lerner et al. 2000; Thornton et al. 2001b). The contamination is associated with a chemical plant, constructed in 1950, which manufactured organic chemicals (primarily phenol, cresols and xylenols) from coal tar. Spillage of these chemicals has produced a plume extending approximately 500m from the site to a depth of 60 mbgs (metres below ground surface), as defined by the 10 mg/L phenol concentration contour during preliminary site investigation. The total concentration of phenolic compounds in the source area is on the order of 25,000 mg/L, roughly half of which is phenol. Mean groundwater flow velocity is 10 m/yr and the water table is 4 mbgs. Site history and groundwater flow patterns suggest that the spillages started soon after construction of the plant; i.e. approximately 1950. There is no information to indicate when and where specific spillages occurred, nor when they stopped. The fact that the plume remains anchored to the source area suggests that a non-aqueous phase liquid (NAPL) is still present in the source area.

The initial investigation of this plume by consultants included the installation of 22 monitoring wells that were fitted with screens between 1m and 10m in length. The location and screen lengths of these monitoring wells are shown in Figure 4. The monitoring network included monitoring wells located upgradient of the site (not shown in Figure 4), two transects of wells across the plume staggered at different depths, and a downstream sentinel monitoring well. Groundwater samples were collected using dedicated bladder pumps and appropriate sample preservation methods were used. The idealised phenol plume (compressed in section from the 3D monitoring well network) is shown in Figure 4b. Additional geochemical data from this sampling event is presented by Williams et al. (2001). These data suggest that phenol concentrations decrease with increasing distance from the source and depth in the aquifer. The contaminant concentrations along the line oriented parallel to groundwater flow described by monitoring wells A, B and C in Figure 4b appear to decrease markedly. Using these data and analytical methods developed for MNA assessments (Wiedemeier et al. 1999), the contaminant concentration data were corrected for dilution and sorption in the plume (by normalizing contaminant concentrations to chloride concentrations), and a plume-scale pseudo-first order degradation rate constant of 0.104 $yr^{-1}$ was calculated for phenol. However, chemically incompatible redox species were observed in some of the monitoring wells (i.e. DO and methane), probably a result of mixing groundwater from different redox zones sampled by the long well screens, suggesting that better vertical resolution of the plume was necessary.

Two high-resolution multilevel samplers (BH59 and BH60) were installed at a distance of 130 m and 350 m from the source area (Figure 4b) to depths of 30 m and 45 m, respectively, to better resolve the

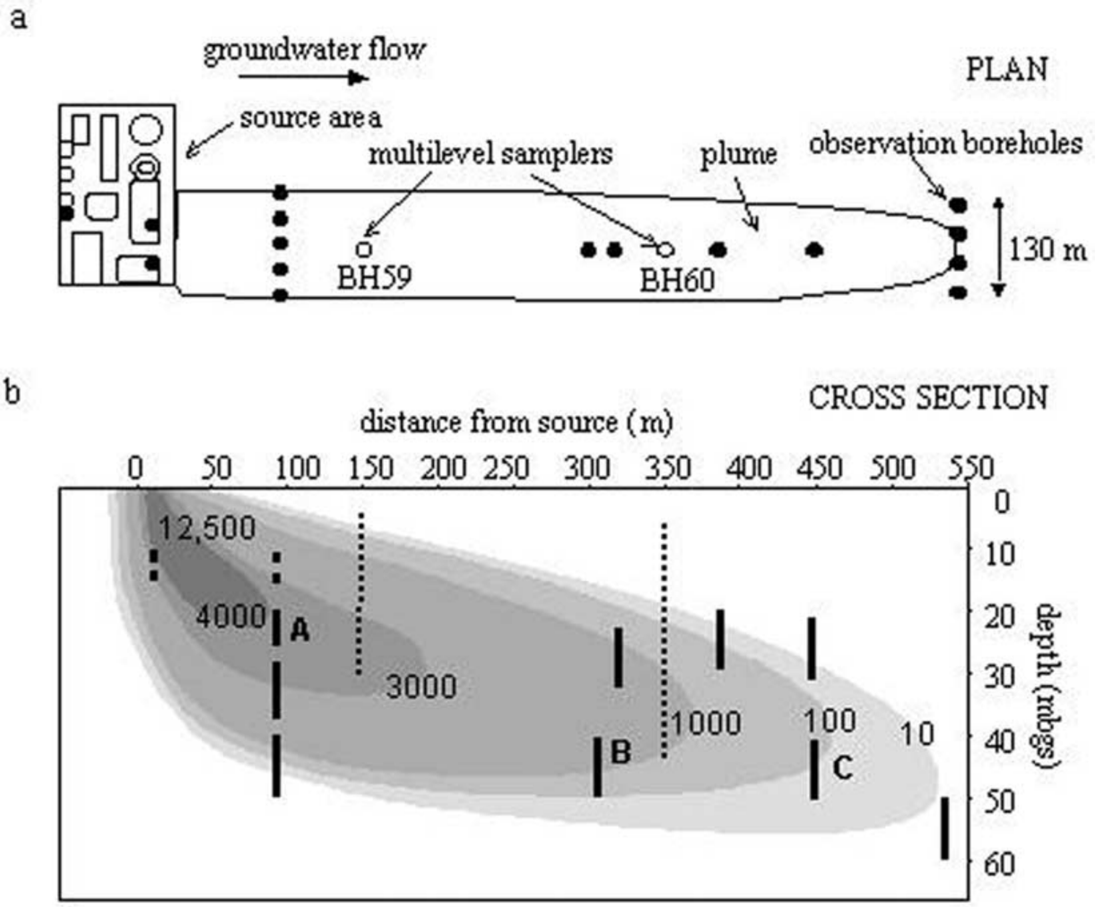

*Figure 4.* Schematic diagrams of the phenolic plume in the West Midlands, UK. (a) plan location of long screen observation wells, multilevel sample wells, and the approximate position of the 10mg/L phenol contour. (b) cross section showing distribution of phenol (mg/L) inferred from concentrations observed in long-screened monitoring wells (indicated by vertical black bars). Concentration data from Williams et al. (2001).

*Table 1.* Contaminant carbon and aquifer oxidant consumption estimated from the MLS profiles

| Species | Oxidant consumption (kg·m$^{-2}$)[1] | | Contaminant consumption (kg phenol-C·m$^{-2}$)[1,2] | | | |
|---|---|---|---|---|---|---|
| | BH59 | BH60 | BH59 | Residual phenol-C | BH60 | Residual phenol-C |
| $O_2$ | 0.42 | 0.21 | 0.14 | | 0.066 | |
| $NO_3$ | 4.67 | 4.2 | 0.97 | | 0.87 | |
| $SO_4$ | 0.0016 | 0.001 | 0.00034 | | 0.00022 | |
| $MnO_2$ | 0.041 | 0.24 | 0.0032 | | 0.018 | |
| FeOOH | 0.15 | 0.24 | 0.0056 | | 0.009 | |
| Acetate | | | 0.31 | | 0.19 | |
| Total | 5.28 | 4.89 | 1.43 | 7.18 | 1.15 | 15.5 |

[1] Values are integrated over the depth of the MLS profile.

[2] Consumption is presented in terms of equivalent phenol carbon and by assuming that all contaminants are present as phenol.

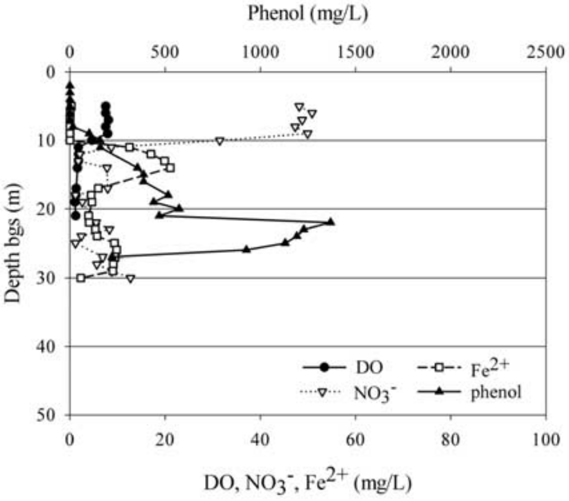

*Figure 5.* Profiles of selected dissolved species at BH59, 130 m from the source. All concentrations are in mg/L.

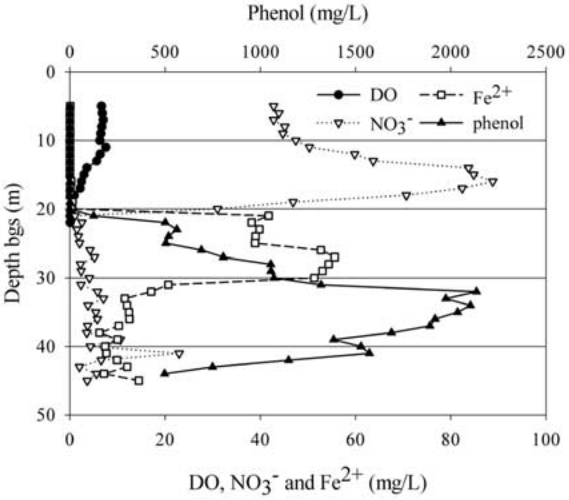

*Figure 6.* Profiles of selected dissolved species at BH60, 350 m from the source. All concentrations are in mg/L.

vertical distribution of contaminants and electron acceptors in the plume. Each multilevel (ML) consisted of a series of 5-cm long sample screens set at 1 m intervals along the total drilled depth (Thornton et al. 2001b). Vertical profiles of phenol and selected redox-sensitive NA indicator species from a May 2002 sample event are plotted in Figures 5 and 6. These profiles suggest a conceptual model of the plume that is quite different from that derived from long-screened well data (e.g. Figure 4b). Contaminants (typified by the phenol data presented) were present over a 20m interval at each borehole location, with markedly higher concentrations within a discrete zone at depth, in contrast to the more homogeneous ~40 m thick plume depicted in the original conceptual model (Williams et al. 2001). The higher contaminant concentrations in the downstream MLS borehole may reflect temporally variable contaminant flux from the source area. Figures 5 and 6 also show that there are steep phenol and electron acceptor concentration gradients over a thin mixing zone at the upper plume fringe at both MLS borehole locations (especially DO, $NO_3^-$, $Fe^{2+}$), suggesting that aerobic respiration and $NO_3^-$ and $Fe^{3+}$ reduction is constrained to that thin fringe. A depth-integrated electron acceptor and carbon mass balance, using the model developed by Thornton et al. (2001a), shows that those three TEA processes account for the vast majority of phenol degradation (Table 1). Within the plume, elevated concentrations of $Mn^{2+}$, $Fe^{2+}$, $S^{2-}$, $CO_2$, $CH_4$, $H_2$, total inorganic carbon (TIC), acetate and the organic metabolites 4-hydroxybenzaldehyde (4HBH) and 4-hydroxybenzoic acid (4HBA) indicate that further biodegradation occurs by $Mn^{4+}$/$Fe^{3+}$-reduction, $SO_4^{2-}$-reduction, methanogenesis and fermentation (data not shown, see Thornton et al. (2001b) for details), but apart from fermentation account for minor carbon turnover. The aforementioned mass balance model was also used to estimate an overall plume-scale pseudo-first order degradation rate of 0.005 $yr^{-1}$, which is two orders of magnitude lower than that obtained using data from the long-screened monitoring wells. In addition to the slow degradation rate, these data also show that the residual contaminant load vastly exceeds the supply of available electron acceptors and, given the presence of a strong source term, suggest that the plume will be long-lived and will grow under the present conditions.

## Discussion

There have been numerous examples, particularly petroleum hydrocarbons, where natural attenuation has been clearly demonstrated using current monitoring strategies (see Wiedemeier et al. (1999) for examples), predominantly because natural biodegradation occurs under all or most redox conditions and rates are typically high. There are almost certainly other cases, such as MTBE and other recalcitrant organics, where natural biodegradation may be limited to one TEAP and/or rates may be lower than can be resolved using these same monitoring strategies. It has been demonstrated that MTBE at Vandenberg Air Force Base degrades aerobically (Wilson et al. 2002) but because the aquifer is naturally anaerobic and exerts significant background oxygen demand, it is currently thought that natural biodegradation, if it occurs at all, is limited to the thin contact zone between the plume and the vadose zone and/or oxygenated recharge water. For degradation to occur, water bearing oxygen and MTBE must mix by typically weak transverse vertical dispersion and diffusion (Smith 1997; Fiori & Dagan 1999). However, the multilevel transect B was not detailed enough to detect such a fringe if indeed it exists. Work at the site continues in order to evaluate alternative monitoring approaches.

The detailed ML data from the phenol plume in the West Midlands clearly show that the degradation processes most responsible for plume attenuation may be confined to a 1–2 m thick zone around the plume fringe. This pattern may be a distinctive feature of plumes containing contaminants that degrade under more than one redox condition (Davis et al. 1999; Schreiber & Bahr 1999; Cozzarelli et al. 1999, 2001; McGuire et al. 2000; Thornton et al. 2001b). Furthermore, fine resolution ML data avoid the confounding interpretations that can be made from data collected in long-screened wells that straddle different redox zones.

In the case of plumes with very large areal extent, it could be argued that since the top and bottom represent the majority of plume surface area, processes occurring there may dominant natural attenuation. Even plumes emanating from modest fuel spills will have surface areas dominated by the top and bottom fringes. As has been shown, TEAPs can be characterised using fine-resolution vertical MLs. If such data is coupled with a general understanding of plume spatial variability and estimates of total mass flux obtained from modest transect instrumentation, only a few ML wells might be necessary. This is especially appealing where contamination occurs deep in rock aquifers that are expensive to instrument.

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