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ADVOCATE bulletin

CL:AIRE's ADVOCATE bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes the plume fringe concept and its role in the biodegradation of contaminant plumes.

The plume fringe: a zone of increased potential for biodegradation in contaminant plumes

1. Introduction

Groundwater contaminated with organic compounds remains a significant threat to the environment and water resources. Monitored natural attenuation (MNA) is a relatively non-invasive and sustainable method for groundwater restoration (Environment Agency, 2000). The successful implementation of MNA requires detailed monitoring and rigorous assessment of the *in situ* processes responsible for contaminant removal and risk reduction (Wilson *et al.*, 2004; Thornton and Rivett, 2008). Groundwater quality data (including hydrogeochemistry and microbiology analysis) are necessary to interpret contaminant fate, redox processes and biodegradation potential in aquifers for the assessment of MNA and other remediation concepts. The spatial variability in redox processes and relative distribution of microbial populations mediating biodegradation is similar in many organic contaminant plumes. The plume core with the highest contaminant mass is usually highly reducing and often characterised by relatively slow anaerobic biodegradation processes (Christensen *et al.*, 2000). In contrast, at the less reducing plume fringe (interface between the plume and background groundwater), *in situ* biodegradation potential is typically enhanced by transverse mixing of contaminants with the background groundwater containing a higher proportion of soluble oxidants (e.g. dissolved oxygen and nitrate) (Thornton *et al.*, 2001a; McGuire *et al.*, 2005). The plume fringe provides optimal conditions for microorganisms to biodegrade organic contaminants (Pickup *et al.*, 2001; Tuxen *et al.*, 2006). In this bulletin the plume fringe concept and its role in the biodegradation of contaminant plumes is presented, using field and laboratory data from two UK sites contaminated with different organic compounds.

2. Conceptual Model

Groundwater in uncontaminated aquifers is often abundant in dissolved electron acceptors (EA) such as oxygen (O_2), nitrate (NO_3^-) and sulphate (SO_4^{2-}), which originate from recharge and mineral dissolution reactions, among other sources (McGuire *et al.*, 2005). Contaminants released into such aquifers from a point source will form a plume with high reducing potential (Christensen *et al.*, 2000). The centre of mass with the highest contaminant concentration is the plume core, characterised by relatively slow anaerobic reactions such as manganese(IV)-reduction, iron(III)-reduction, sulphate-reduction, methanogenesis and fermentation (Christensen *et al.*, 2000). Low microbial activity in the plume core may be due to contaminant toxicity, concentration effects or chemical diversification (Thornton *et al.*, 2001b; Tischer *et al.*, 2013). At the plume boundaries background groundwater mixes with contaminants by dispersion, which dilutes their concentration locally and introduces dissolved oxidants into the plume (Thornton *et al.*, 2001b; Bauer *et al.*, 2008). This creates conditions for enhanced biodegradation, often dominated by aerobic respiration and denitrification. The plume fringe is characterised by increased cell numbers and enhanced microbial activity (Pickup *et al.*, 2001; Tuxen *et al.*, 2006). A simplified conceptual model of an organic contaminant plume, including the distribution of plume fringe and plume core processes, is presented in Figure 1.

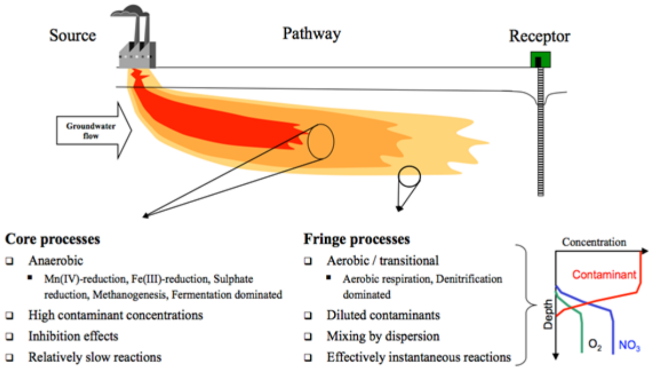

Figure 1. Conceptual model of organic contaminant plume showing distribution of core and fringe biodegradation processes. Uncontaminated groundwater provides dissolved oxidants to support the fringe biodegradation processes. The insert on the lower right shows the vertical distribution of dissolved chemical species in groundwater, which defines the location and extent of the (lower) plume fringe. The same vertical distribution but in reverse profile would define the upper plume fringe.

3. Case Study No.1

The site is an organic chemical manufacturing plant located on the Permo-Triassic sandstone aquifer. The contaminant plume consists of mainly phenol, cresols and xylenols. Multilevel samplers (MLSs) were installed at two locations (130 m and 350 m from the source) along the plume flow path to depths of 30 m and 45 m below ground level (mbgl). These installations provide monitoring of groundwater quality at 1 m depth-discrete intervals (full description in Lerner *et al.*, 2000; Williams *et al.*, 2001; Thornton *et al.*, 2001b).

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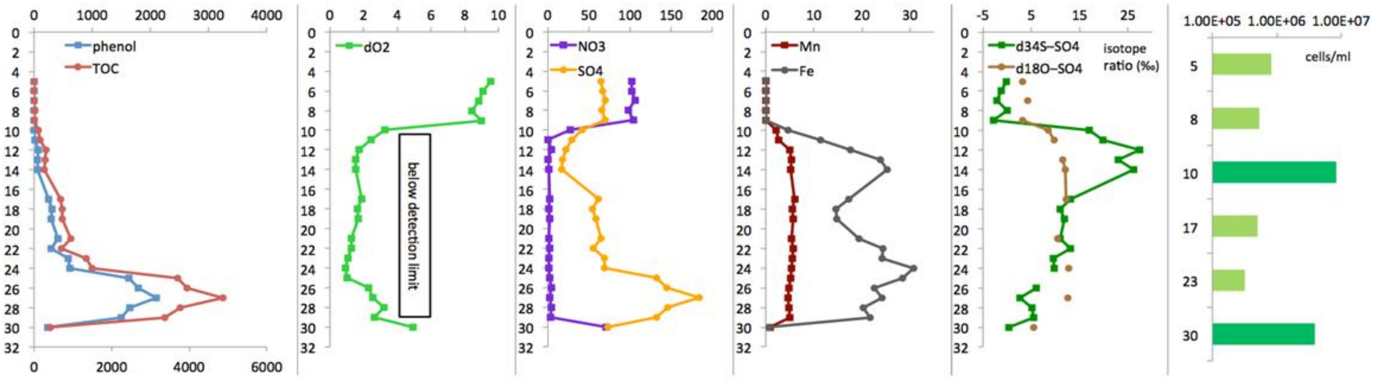

Figure 2. Vertical profiles of selected species in groundwater 130 m from the source. All concentrations are in mg/l unless stated otherwise. The vertical axes represent mbgl. Graphs modified after Thornton *et al.* (2001b), Pickup *et al.* (2001) and Spence *et al.* (2001).

Vertical profiles of dissolved compounds in groundwater at 130 m from the source, including phenol, total organic carbon (TOC), O_2, NO_3^-, SO_4^{2-}, Mn(II), Fe(II), sulphate–oxygen and sulphate–sulphur isotope data, and numbers of microorganisms are presented in Figure 2. The water table is at 5 mbgl. The upper fringe of the plume is approximately 10 mbgl and the lower fringe is approximately 30 mbgl at this location. Background groundwater contains O_2, NO_3^- and SO_4^{2-}. Due to measurement interferences with the organic matrix, the O_2 concentration is assumed to be zero in the plume (Thornton *et al.*, 2001b). The elevated SO_4^{2-} concentration in the plume reflects mineral acid releases (Thornton *et al.*, 2001b). Dissolved Mn(II) and Fe(II) are above background groundwater concentrations in the plume. The organic contaminants are below detection from 5 to 10 mbgl, then present from 11 to 30 mbgl with heterogeneous distribution. Sulphate reduction has enriched residual sulphate in ^{34}S in the plume, between 10 and 14 mbgl. The total number of bacteria varies from 2 x 10^5 to 7 x 10^6 cells/ml, with peaks at both plume fringes (10 and 30 mgbl).

4. Case Study No.2

The site is a release of unleaded petroleum fuel containing mainly benzene, toluene, ethylbenzene and xylene (BTEX) and ether oxygenates compounds such as MTBE, located on the Upper Chalk aquifer. Contamination of the saturated zone with these compounds occurs at 20-30 m depth, with the BTEX plume restricted to 125 m from the source and an oxygenate plume extending 220 m downgradient from the source. MLS monitoring wells were installed to determine the distribution of dissolved contaminants in the saturated zone and evaluate the natural attenuation of these plumes (Wealthall *et al.*, 2001, 2002; Spence and Thornton, 2003; Spence *et al.*, 2005).

Figure 3 shows vertical profiles of the main organic contaminant groups (MTBE, BTEX), dissolved electron acceptors (O_2, NO_3^-, SO_4^{2-}) and products of contaminant biodegradation (dissolved Mn(II), Fe(II) and total dissolved inorganic carbon (TDIC)) in groundwater. The water table is approximately 22 mbgl. Most of BTEX compounds are attenuated near the source, with benzene apparently less biodegradable under the existing anaerobic conditions (Figure 3a). The MTBE plume has migrated further from the source. The distribution of dissolved electron acceptors and biodegradation products reveals a zonation in the BTEX and MTBE plumes (Figure 3b and 3c). Conditions near the source are highly reducing, with

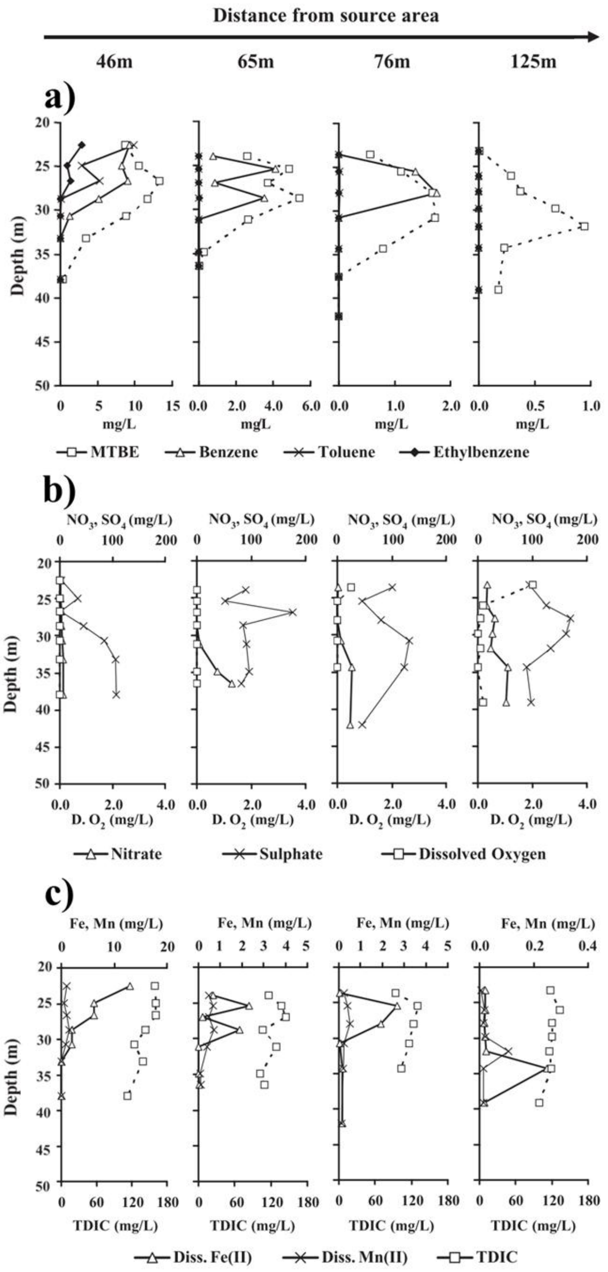

Figure 3. Vertical profiles of a) MTBE and selected contaminant species, b) dissolved electron acceptors (O_2, NO_3^-, SO_4^{2-}), c) products of contaminant biodegradation (dissolved Mn(II), Fe(II), TDIC) in groundwater at different distances from the source. Graphs modified after Spence *et al.*, (2005).

consumption of electron acceptors and corresponding increased concentrations of dissolved Mn(II) and Fe(II) in groundwater (46m, Figure 3b and 3c). Further downstream the trend is opposite; dissolved Mn(II) and Fe(II) are present at much lower concentration and the concentration of dissolved electron acceptors is higher (125m, Figure 3b and 3c). Elevated TDIC in the plume reflects inorganic carbon from biodegradation processes (Figure 3c). The upper fringe of the plume at this site is defined by the presence of O_2 and absence of organic contaminants at shallow depth (approximately 23 mbgl), whereas the lower fringe of the plume is captured by the decreased organic contaminants but increased O_2 and NO_3^- (approximately 38-40 mbgl).

In addition to the field studies, Shah *et al.* (2009) investigated the potential for MTBE biodegradation in groundwater at the site using microcosm experiments maintained under *in situ* conditions. Figure 4 shows results from experiments with contaminated groundwater and uncontaminated aquifer sediment from outside the MTBE plume. MTBE was added at 1 mg/l concentration, with a 2 mg/l O_2 concentration as the starting condition, to represent the plume fringe zone. The initial fall in O_2 concentration represents an equilibration phase (Figure 4b). The arrows show biodegradation of MTBE occurred with O_2 depletion between 15 and 33 days and 131 and 166 days. At the 2nd MTBE addition (indicated by the broken line), the O_2 concentration was 0.68 mg/l and 0.84 mg/l in microcosms A-1.0a and A-1.0b, respectively. The relatively low O_2 concentration did not affect MTBE metabolism and the biodegradation potential of the intrinsic microorganisms (Figure 4a).

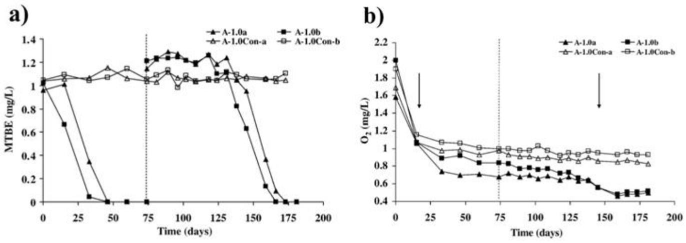

Figure 4. a) Aerobic biodegradation of MTBE in microcosms containing 2 mg/l dissolved O_2 and 1 mg/l initial concentration of MTBE, re-added as shown by the broken vertical line. b) Measured O_2 concentration in the microcosms. Closed markers are live replicates, while open markers are killed controls. Graphs adapted from Shah *et al.* (2009).

5. Discussion

The plume fringe at the site contaminated with phenols has steep vertical gradients in dissolved O_2 and NO_3^- concentration. The plume fringe appears to be 2 m thick, but this observation reflects the resolution of the MLS used and in many cases this interface is considerably less than in the example presented. Depletion of these electron acceptors occurs at the same depth as the contaminants (Figure 2). Aerobic respiration and denitrification occur concomitantly at the plume fringes, and is followed in the plume by sulphate reduction at shallow depth (isotope data, Figure 2). Despite available SO_4^{2-} in the plume core, biodegradation is limited in this zone by the contaminant concentrations (Lerner *et al.*, 2000; Thornton *et al.*, 2001b). Thus, biodegradation processes at the plume fringe are responsible for most of the contaminant mass removal (Table 1).

The aquifer at the petroleum fuel release site is fractured, resulting in complex contaminant transport (Spence and Thornton, 2003). The plume fringe, where MTBE in the plume and aerobic groundwater are expected to mix, is not resolved in detail in this example. This is due to the sample port spacing on the MLS installations and fracture spacing in the aquifer (Spence *et al.*, 2005). Therefore, the laboratory microcosm experiments were undertaken to examine MTBE biodegradation at the groundwater-plume interface and explore the plume fringe concept in this aquifer (Shah *et al.*, 2009; Thornton *et al.*, 2011). The microcosm experiments using aquifer materials from the site confirmed that the aquifer microorganisms can biodegrade MTBE under the plume fringe conditions (Figure 4). Although not easily observed at the field-scale, due to the complex aquifer hydrogeology and MLS resolution (only seven sampling ports in each MLS), the results show that aerobic biodegradation at the plume fringe can effectively attenuate MTBE in the plume (Shah *et al.*, 2009; Thornton *et al.*, 2011).

Table 1. Mass balance for oxidant and organic contaminant consumption at 130 m and 350 m from the source, calculated using the MLS data and methodology in Thornton *et al.* (2001a).

Species	Oxidant consumption (tonnes)		Phenol consumption (tonnes)	
	130 m	350 m	130 m	350 m
O_2	**29**	**14.5**	**12.2**	**6.1**
NO_3^-	**321**	**289**	**87**	**78**
SO_4^{2-}	0.11	0.07	0.031	0.019
MnO_2	2.85	16.6	0.22	1.28
FeOOH	10.3	16.5	0.39	0.62
*CH_3COO^-			27.7	17.2
	363	337	128	103
*Fermentation via reaction: $C_6H_6O + 5H_2O$ -> $3CH_3COOH + 6H_2$				

Both case studies show that biodegradation is most pronounced at the boundaries of contaminant plumes, where dissolved electron acceptors (O_2, NO_3^-) mix with and dilute organic contaminants. The plume fringe concept has also been proven at other sites contaminated with petroleum hydrocarbons (Takahata *et al.*, 2006; Winderl *et al.*, 2008; Anneser *et al.*, 2008, 2010; Jobelius *et al.*, 2011), chlorinated solvents (only for cis-DCE, VC; Witt *et al.*, 2002; Davis *et al.*, 2002) and landfill leachate (Tuxen *et al.*, 2006). Jobelius *et al.* (2011) found that the peak concentration of BTEX metabolites in a tar oil-contaminated aquifer corresponded with the upper plume fringe location, although it was not possible to quantify the biodegradation rate of particular compounds. Other studies of a leachate-contaminated aquifer have confirmed an enhanced biodegradation potential at the plume fringe, with increased presence of specific microorganisms responsible for biodegradation of organic contaminants (Tuxen *et al.*, 2006). In all cases it is important to note that the analysis of biodegradation processes at the plume fringe cannot be achieved using single screen monitoring wells (Wilson *et al*, 2004). Instead, the clear definition of this interface and interpretation of redox processes, microbial dynamics and contaminant fate across it requires the use of high-resolution MLS monitoring wells, as illustrated in the two case studies. These studies and the supporting literature show that the plume fringe concept is valid for different aquifer settings and contaminant groups. Greater attention should be given to the assessment of contaminant biodegradation at this interface in plumes where MNA and other remediation strategies are implemented at sites.

6. Conclusion

The case studies illustrate a new way of thinking about monitoring and interpreting biodegradation processes in plumes, which provides increased confidence in the assessment of contaminant fate as a cornerstone for decision-making on environmental risk assessment and design of remediation strategies to manage groundwater pollution. They highlight the need to focus research on overlapping zones at the plume fringes and at the plume core. High precision MLS monitoring wells with sub-metre vertical intervals can reveal small-scale vertical heterogeneities in redox zones and biodegradation processes needed to correctly interpret the fate of organic contaminants in plumes. Those, together with existing comprehensive models like the CORONAScreen for MNA (http://corona.group.shef.ac.uk) provide an improved basis for the assessment of natural attenuation in plumes.

7. Acknowledgements

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