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Enhancement of *in situ* biodegradation of organic compounds in groundwater by targeted pump and treat intervention

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A B S T R A C T

This study demonstrates the value of targeted pump and treatment (PAT) to enhance the *in situ* biodegradation of organic contaminants in groundwater for improved restoration. The approach is illustrated for a plume of phenolic compounds in a sandstone aquifer, where PAT is used for hydraulic containment and removal of dissolved phase contaminants from specific depth intervals. Time-series analysis of the plume hydrochemistry and stable isotope composition of dissolved species ($\delta^{34}S$-SO_4, $\delta^{13}C$-CH_4, $\delta^{13}C$-TDIC (TDIC = Total Dissolved Inorganic Carbon)) in groundwater samples from high-resolution multilevel samplers were used to deduce changes in the relative significance of biodegradation processes and microbial activity in the plume, induced by the PAT system over 3 years. The PAT system has reduced the maximum contaminant concentrations (up to 6800 mg L^{-1} total phenols) in the plume by 50% to ~70% at different locations. This intervention has (i) stimulated *in situ* biodegradation in general, with an approximate doubling of contaminant turnover based on TDIC concentration, which has increased from <200 mg L^{-1} to >350 mg L^{-1}, (ii) enhanced the activity of SO_4-reducing microorganisms (marked by a declining SO_4 concentration with corresponding increase in SO_4-$\delta^{34}S$ to values >7–14‰$_{V\text{-}CDT}$ relative to background values of 1.9–6.5‰$_{V\text{-}CDT}$), and (iii) where the TDIC increase is greatest, has changed TDIC-$\delta^{13}C$ from values of −10 to −15‰$_{V\text{-}PDB}$ to ~−20‰$_{V\text{-}PDB}$. This indicates an increase in the relative importance of respiration processes (including denitrification and anaerobic methane oxidation, AMO) that yield ^{13}C-depleted TDIC over fermentation and acetoclastic methanogenesis that yield ^{13}C-enriched TDIC in the plume, leading to higher contaminant turnover. The plume fringe was found to be a zone of enhanced biodegradation by SO_4-reduction and methanogenesis. Isotopically heavy methane compositions (up to −47.8‰$_{V\text{-}PDB}$) and trends between $\delta^{13}C$-TDIC and $\delta^{13}C$-CH_4 suggest that AMO occurs at the plume fringe where the contaminant concentrations have been reduced by the PAT system. Mass and isotope balances for inorganic carbon in the plume confirm the shift in spatial dominance of different biodegradation processes and significant increase in contribution of anaerobic respiration for contaminant biodegradation in zones targeted by the PAT system. The enhanced *in situ* biodegradation results from a reduction in organic contaminant concentrations in the plume to levels below those that formerly suppressed microbial activity, combined with increased supply of soluble electron acceptors (e.g. nitrate) into the plume by dispersion. An interruption of the PAT system and recovery of the dissolved organic contaminant concentrations towards former values highlights the dynamic nature of this enhancement on restoration and relatively rapid response of the aquifer microorganisms to changing conditions induced by the PAT system. *In situ* restoration using this combined engineered and passive approach has the potential to manage plumes of biodegradable contaminants over shorter timescales than would be possible using these methods independently. The application of PAT in this way strongly depends on the ability to ensure an adequate flux of dissolved electron acceptors into the plume by advection and dispersion, particularly in heterogeneous aquifers.

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1. Introduction

Phenols (e.g. phenol and cresols) and their derivatives occur naturally in the environment but have also been produced commercially for use in many products. Many industrial activities, such as wood preservation and tannery facilities, fossil fuel refining processes, manufactured gas plants, pesticide and pharmaceutical production also create phenolic compounds as a by-product of their respective processes (Pereira et al., 1983; Kumaran and Paruchuri, 1997; Squillace et al., 1999; Broholm and Arvin, 2000; van Schie and Young, 2000; Broholm and Arvin, 2001; Michalowicz and Duda, 2007; Al-Khalid and El-Naas, 2012). Phenols have important antimicrobial properties, which have medical uses, but can be harmful with the potential to cause acute health affects (Bruce et al., 1987; Tsutsui et al., 1997; Goddard and McCue, 2001; Michalowicz and Duda, 2007) and pose an environmental hazard (Al-Khalid and El-Naas, 2012; Lin et al., 2012). Consequently, the release of these organic chemicals into groundwater from industrial activities will usually require appropriate restoration strategies. Pump and treatment (PAT) is a long-established and widely-used engineered restoration technique for contaminated groundwater (McKinney, 1992; US EPA, 1996; Cohen et al., 1997; Matott et al., 2006; Champagne et al., 2012), in which contaminated groundwater is pumped from an aquifer for *ex situ* treatment by chemical and biological processes (Suthersan, 1999; Simon et al., 2002; Champagne et al., 2012). Other applications of PAT include the injection of chemical reagents to enhance removal of adsorbed and free-phase organic contaminants (Palmer and Fish, 1992; Suthersan, 1999). PAT is also implemented for hydraulic containment to control the migration of contaminated groundwater, preventing continued expansion of the contaminant zone or plume (McKinney, 1992; US EPA, 1996; Cohen et al., 1997; Suthersan, 1999; Matott et al., 2006). In this respect, PAT can be very effective for the management of contaminant plumes which are present at a scale or depth in aquifers that extend beyond the technical feasibililty or range of other engineered interventions.

Biodegradation processes which occur naturally in contaminated groundwater have been used for many years to support risk-based restoration concepts such as natural attenuation (NA) and *in situ* bioremediation (Wiedemeier et al., 1999). Using aqueous and mineral electron acceptors in aquifers indigenous microorganisms can biotransform a wide range of organic chemicals in contaminated groundwater, via pathways which include aerobic respiration, denitrification, sulphate-reduction, methanogenesis and fermentation (Bradley, 2000; Major et al., 2002; Spence et al., 2005). However, the spatial and temporal distribution of these biodegradation processes and, in turn, the metabolic activity of the microorganisms responsible can be influenced significantly by the availability of suitable electron acceptors and nutrients, as well as specific effects related to the contaminant matrix (e.g. chemical composition, concentration of individual compounds and substrate bioavailability) (Broholm and Arvin, 2000; Spence et al., 2001a,b; Haack et al., 2004; Al-Khalid and El-Naas, 2012; Baker et al., 2012). These effects can consequently control the location, extent and relative rates of contaminant turnover in plumes (Schreiber and Bahr, 1999; Lerner et al., 2000; Thornton et al., 2001a,b; Kota et al., 2004; Wilson et al., 2004; Tuxen et al., 2006). The ability to modify the hydrochemical conditions in plumes, by alleviating limitations on microbial metabolism, may offer the opportunity to enhance the biodegradation of organic contaminants *in situ*. However, it is well known that increasing the microbial conversion capacity will not lead to higher biodegradation rates when mass transfer is a limiting factor (Boopathy, 2000). For example, it is usually necessary to increase the supply or bioavailability of substrates required for microbial growth and activity to enhance *in situ* biodegradation. For groundwater plumes this has often been achieved by introducing soluble electron acceptors, electron donors and nutrients into contaminated aquifers to stimulate the activity of indigenous microorganisms, either by direct injection of these amendments or passive addition using technologies such as permeable reactive barriers (Semprini et al., 1990; Bedient and Rifai, 1992; Cunningham et al., 2001; Major et al., 2002; Zhang et al., 2009; Lin et al., 2012). Combining engineered and passive technologies for groundwater restoration is a novel but under-utilised management approach (e.g. Haas, 1997; Dettmers et al., 2006). It offers the potential for more complete treatment of contaminated groundwater *in situ* and achievement of restoration objectives in timeframes which may not be possible using one technique. The integration of PAT with NA and bioremediation for the management of contaminated groundwater has seldom been considered in practice, since these approaches have a different technical objective. PAT is typically used to simply remove contaminated groundwater from aquifers, whereas NA and bioremediation are used to treat contaminants *in situ*. In the research described in this study, PAT has been implemented in a targeted manner at field-scale to remove organic contaminants from specific depths in the aquifer, as a basis to enhance the *in situ* treatment of the residual contaminants by NA. It can be envisaged that perturbation of the plume by the PAT system in this way could also negatively affect the activity and function of indigenous microbial populations which have adapted to the *in situ* conditions. Potential effects include the mixing of groundwater with different redox status (aerobic vs anaerobic), contaminant concentration and pH, which may result in substrate starvation and suppression of metabolic function of specific microorganisms (Harrison and Loveless, 1971; Karthikeyan et al., 2001; Chakraborty et al., 2010). This is undesirable if such changes reduce biodegradation rates, lower contaminant turnover and decrease treatment efficiency. Moreover, the timescale for adaptation of the *in situ* microbial community to the imposed conditions and re-establishment of optimum metabolic activity may limit the overall performance of the engineered restoration, if this occurs over a longer period than the amendment (e.g. the rate of groundwater abstraction in the case of PAT).

In this paper we investigate the contribution of targeted PAT to enhance the *in situ* biodegradation of organic contaminants in groundwater for improved restoration performance. This approach is examined using a PAT system installed for hydraulic containment and treatment of a plume of phenolic compounds in a sandstone aquifer. The spatial distribution of microbially-mediated terminal electron accepting processes (TEAPs) and microbiological activity in this plume is influenced significantly by the availability of dissolved electron acceptors and concentration of the phenols (Lerner et al., 2000; Pickup et al., 2001). Biodegradation of the phenols is sensitive to the organic contaminant concentration and suppressed at certain concentrations (Harrison et al., 2001; Wu et al., 2002, 2006). Specifically, aerobic respiration and denitrification are restricted to a narrow zone at the plume fringe, SO_4-reduction is suppressed within the plume at a contaminant concentration above 2000 mg L^{-1} and fermentation processes are more important for mass turnover at higher contaminant concentrations (Thornton et al., 2001a,b; Spence et al., 2001b; Wu et al., 2002, 2006; Baker et al., 2012). This conceptual model of contaminant biodegradation potential in the plume has remained consistent since 2001. It informed the design of the PAT system, which has been operated to remove groundwater from specific depths in the plume, where biodegradation is inhibited by the contaminant concentrations. This conceptual model can thus be tested by examining the change in the distribution of TEAPs, caused by the PAT