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Aerobic bioremediation of 1,2 dichloroethane and vinyl chloride at field scale

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ABSTRACT

Aerobic bioremediation of 1,2 dichloroethane (1,2 DCA) and vinyl chloride (VC) was evaluated at field scale in a layered, silty and fine-sand anaerobic aquifer. Maximum concentrations of 1,2 DCA (2 g/L) and VC (0.75 g/L) in groundwater were within 25% and 70% of pure compound solubility, respectively. Aerobic conditions were induced by injecting air into sparging wells screened 20.5–21.5 m below ground (17–18 m below the water table). Using a cycle of 23 h of air injection followed by three days of no air injection, fifty days of air injection were accumulated over a 12 month period which included some longer periods of operational shutdown. Oxygen and volatile organic compound probes, and multilevel samplers were used to determine changes of the primary contaminants and the associated inorganic chemistry at multiple locations and depths. Air (oxygen) was distributed laterally up to 25 m from the sparge points, with oxygen partial pressures up to 0.7 atmospheres (28–35 mg/L in groundwater) near to the sparge points. The dissolved mass of 1,2 DCA and VC was reduced by greater than 99% over the 590 m^2 trial plot. Significantly, pH declined from nearly 11 to less than 9, and sulfate concentrations increased dramatically, suggesting the occurrence of mineral sulfide (e.g., pyrite) oxidation. Chloride and bicarbonate (aerobic biodegradation by-products) concentration increases were used to estimate that 300–1000 kg of chlorinated hydrocarbons were biodegraded, although the ratio of 1,2 DCA to VC that was biodegraded remained uncertain. The mass biodegraded was comparable but less than the 400–1400 kg of chlorinated compounds removed from the aqueous phase within a 10,000 m^3 volume of the aquifer. Due to the likely presence of non-aqueous phase liquid, the relative proportion of volatilisation compared to biodegradation could not be determined. The aerobic biodegradation rates were greater than those previously estimated from laboratory-based studies.

1. Introduction

The chlorinated hydrocarbons 1,2 dichloroethane (1,2 DCA) and vinyl chloride (VC) are common groundwater contaminants at petrochemical plants (Janssen et al., 1994; De Wildeman et al., 2003). At such sites, petroleum compounds (e.g., benzene) are precursors in the production of 1,2 DCA, which is a feedstock for the manufacture of VC monomers. 1,2 DCA has also been used as a lead scavenger in fuels (Falta, 2004). As a pure phase, 1,2 DCA is a dense non-aqueous phase liquid (DNAPL) with a solubility of 7600 mg/L (Lide, 2000), whereas VC has a solubility of 1100 mg/L (ChemFinder, 2004). Often 1,2 DCA and VC are co-disposed but VC can also be a degradation product of 1,2 DCA under alkaline conditions (Nobre and Nobre, 2004).

There is evidence that 1,2 DCA will transform abiotically, and biodegrade under both aerobic and anaerobic conditions (Egli et al., 1987; Barbash and Reinhard, 1989; Klečka et al., 1998). Aerobic degradation was reported only after 2 years of incubation and significant degradation only occurred after 5 years in an above ground treatment system (Stucki et al., 1992; Stucki and Thuer, 1995). Under aerobic conditions, 1,2 DCA degraded to carbon dioxide in one of three freshly-spiked/previously-contaminated soils following a lag period of 13 weeks incubation (Klečka et al., 1998). Even so, the mass removal after

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18 weeks was minimal (~5%) compared to controls. To date, most studies of aerobic 1,2 DCA biodegradation have employed enriched or pure cultures (Stucki et al., 1983; Janssen et al., 1985; Hage and Hartmans, 1999; Hunkeler and Aravena, 2000; Hirschorn et al., 2007), rather than soils from contaminated sites. Isotope studies have been employed to quantify 1,2 DCA biodegradation under aerobic conditions (Hirschorn et al., 2007). It is generally accepted that VC will biodegrade under aerobic conditions (Chu et al., 2004; Sing et al., 2004).

The intrinsic biodegradation of 1,2 DCA in groundwater has been studied at industrial sites (Bosma et al., 1997; Lee et al., 1999; Wycisk et al., 2003; Nobre and Nobre, 2004). Typically, remediation trials for 1,2 DCA contamination have used anaerobic electron acceptor or carbon electron donor amendments (Lu et al., 2002; Dyer et al., 2003; Hoekstra et al., 2004), perhaps because earlier studies indicated that aerobic biodegradation of 1,2 DCA could be slow. Investigations utilising carbon amendments have frequently encountered difficulties with blockage of well screens and reduction in groundwater flow (Dyer et al., 2003). Also, little attenuation of 1,2 DCA was found using a zero-valent iron permeable reactive barrier (Lai et al., 2006).

Whilst the evidence for aerobic biodegradation of 1,2 DCA from the published literature is not extensive, it is appealing as a bioremediation strategy since aerobic conditions can also stimulate the biodegradation of associated petroleum hydrocarbon compounds, such as benzene. Consequently, successful aerobic biodegradation could eliminate the need for potentially expensive and complex dual treatment strategies (such as sequential electron donor and oxygen amendments) for sites contaminated with 1,2 DCA, VC and petroleum compounds. Here we describe a field-scale evaluation of aerobic bioremediation for 1,2 DCA and VC in the presence of petroleum hydrocarbons. The aims of the work were (i) to devise and show the successful delivery of oxygen into the subsurface to create aerobic conditions deep (17–18 m) below the water table that were conducive to aerobic biodegradation of 1,2 DCA, VC and petroleum hydrocarbons; (ii) to quantify mass losses of the primary contaminants over the entire depth profile of the contaminated aquifer and over a lateral distance of significance if scale-up were attempted, and (iii) to quantify the role of aerobic biodegradation in achieving such contaminant mass losses from the groundwater. As far as the authors can determine, no previous data are available to show significant aerobic biodegradation of 1,2 DCA, and no field demonstration or evaluation of enhanced aerobic bioremediation has been previously published.

2. Field site and methods

2.1. Site and aeration strategy

The field site is located at a petrochemical plant where petroleum compounds (e.g., benzene) were used in the production of 1,2 DCA for the subsequent manufacture of VC. Groundwater was typically 2.5–3.0 m below ground surface with flow rates estimated to be in the range 20–100 m/year. Generally at the field site, 1,2 DCA, VC and petroleum hydrocarbon compounds (primarily benzene) contaminated groundwater to depths of 20–30 m below ground surface. The 20–25 m thick saturated zone of the aquifer was comprised of sandy silt with some clay layers. Locally, 1,2 DCA and VC had peak concentrations of 1–2 g/L at depths of 17–21 m, whilst benzene had peak concentrations of 200 mg/L at 6–10 m below ground surface. Other chlorinated organic compounds were found at much lower concentrations. For example, the maximum concentration of 1,1,2,2 tetrachloroethane was 2.7 mg/L, 1,1,2 trichloroethane was 28 mg/L, 1,1 dichloroethane was 1 mg/L, cis-1,2 dichloroethene was 4.7 mg/L and trichloroethene was 4.1 mg/L.

The aeration strategy was designed to inject air at the base of the aquifer, 20.5–21.5 m below ground (approximately 17–18 m below the water table) where the highest concentrations were measured. Since the target contaminants are volatile, volatilisation was expected along with biodegradation. Six air injection points were installed across the groundwater flow direction (Fig. 1) at 4 m intervals. The

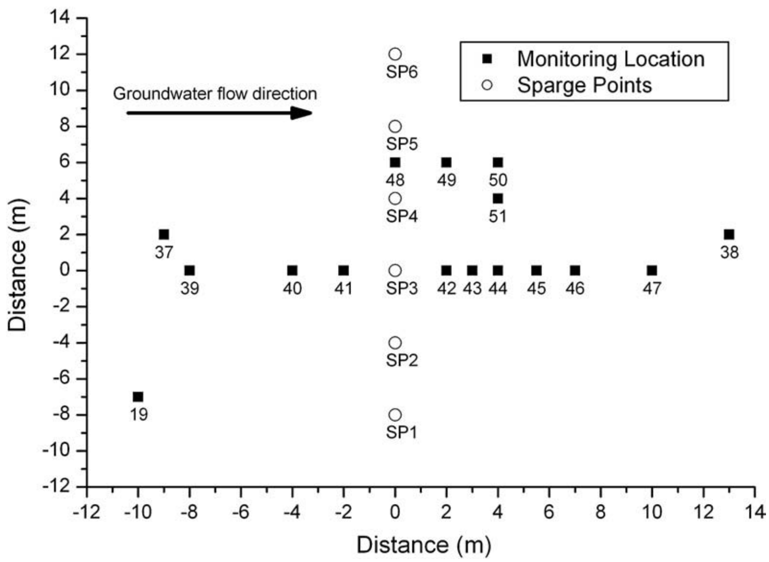

Fig. 1. Layout of sparge points (SP1-6), and monitoring locations (Note: MWSA locations are denoted as numbers only). BH151 (not shown) is located at the approximate (x, y) coordinates (-10 m, -18.2 m).