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ZVI-Clay remediation of a chlorinated solvent source zone, Skuldelev, Denmark: 2. Groundwater contaminant mass discharge reduction

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ABSTRACT

The impact of source mass depletion on the down-gradient contaminant mass discharge was monitored for a 19-month period as a part of a field demonstration of the ZVI-Clay soil mixing remediation technology. Groundwater samples were collected from conventional monitoring wells (120 samples) and a dense network of multilevel samplers (640 samples). The hydraulic gradient and conductivity were determined. Depletion of the contaminant source is described in the companion paper (Fjordbøge et al., 2012). Field data showed four distinct phases for PCE mass discharge: (1) baseline conditions, (2) initial rapid reduction, (3) temporary increase, and (4) slow long-term reduction. Numerical modeling was utilized to develop a conceptual understanding of the four phases and to identify the governing processes. The initial rapid reduction of mass discharge was a result of the changed hydraulic properties in the source zone after soil mixing. The subsequent phases depended on the changed accessibility of the contaminant mass after mixing, the rate of source depletion, and the concentration gradient at the boundaries of the mixed source zone. Overall, ZVI-Clay soil mixing resulted in a significant down-gradient contaminant mass discharge reduction (76%) for the parent compound (PCE), while the overall reduction of chlorinated ethenes was smaller (21%).

1. Introduction

Chlorinated solvents in the form of dense non aqueous phase liquids (DNAPLs) are long-term sources of contaminated down-gradient groundwater at numerous old industrial sites (Doherty, 2000). Traditionally, ground water quality standards are used as a key metric for risk assessment and remedial performance. However, in recent years there has been an increasing consensus that contaminant mass discharge may be a more appropriate metric at complex DNAPL sites (Basu et al., 2006; Falta et al., 2005a; Jawitz et al., 2005). Mass discharge from the source zone is the driver for the development of the down-gradient contaminant plume and so it is better than concentration measurements for describing the severity of contamination and the changes in the risk to down-gradient receptors (e.g., Basu et al., 2006; Brooks et al., 2008; Einarson and Mackay, 2001; Guilbeault et al., 2005; Jawitz et al., 2005; Soga et al., 2004; Troldborg et al., 2008).

Established *in situ* remediation technologies most often only result in partial source mass depletion (DiFilippo and Brusseau, 2008; McGuire et al., 2006). While the *in situ* remediation technologies may have an immediate impact on contaminant mass in the source zone, the down-gradient response may be less evident. An improved understanding of the relationship between source mass depletion and down-gradient mass discharge reduction is important for assessment of risk and remedial performance at contaminated sites.

The coupling of source mass depletion and down-gradient mass discharge has been investigated in a number

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of studies including mathematical modeling, bench-scale studies and field investigations (e.g., Basu et al., 2006; Brooks et al., 2008; Chambon et al., 2010; Chen and Jawitz, 2009; Christ et al., 2010; DiFilippo and Brusseau, 2008; Falta, 2008; Falta et al., 2005a, 2005b; Fure et al., 2006; Jawitz et al., 2005; Kaye et al., 2008; Liang and Falta, 2008; Newell and Adamson, 2005; Zhu and Sykes, 2004). Various approaches have been suggested for the assessment of the relationship between the down-gradient mass discharge and the mass depletion in the source zone; one of these approaches is a simple analytical power law model (Basu et al., 2006; Falta et al., 2005a; Zhu and Sykes, 2004).

The effect of partial source mass depletion is dependent on site specific conditions such as the source architecture and the flow field heterogeneity (Basu et al., 2008; Chen and Jawitz, 2008; DiFilippo and Brusseau, 2008; DiFilippo et al., 2010; Fure et al., 2006; Jawitz et al., 2005). The type of remediation technology used to obtain source mass depletion will also be of importance. The various types of aggressive *in situ* remediation technologies will have different impacts on the chemical and hydraulic properties of the source zone. However, without more extensive field studies on the different remediation technologies it is difficult to compare and predict the resulting reduction in mass discharge. Studies on mass discharge have included cosolvent/surfactant flushing (e.g., Brooks et al., 2004, 2008; Christ et al., 2006, 2009; Jawitz et al., 2005), chemical oxidation (e.g., Brusseau et al., 2007, 2011; Rivett and Feenstra, 2005), thermal treatment (e.g., Brooks et al., 2008) and enhanced biodegradation (e.g., Chambon et al., 2010).

To date, no investigations have reported on the change of mass discharge following the field application of ZVI-Clay soil mixing. ZVI-Clay soil mixing is a relatively new technology for *in situ* source zone remediation. The technology significantly changes the hydraulic and chemical properties of the source through soil mixing with the addition of zero valent iron (ZVI) and clay. ZVI results in a significant source mass depletion as described in the companion paper (Fjordbøge et al., 2012). The source mass depletion has also been the primary focus of previous field applications (Bozzini et al., 2006; Ovbey et al., 2010; Shackelford et al., 2005). Apart from the source depletion, the ZVI-Clay soil mixing technology is suggested to significantly reduce the down-gradient mass discharge by reducing the hydraulic conductivity of the source.

The main objective of this study was to investigate changes to down-gradient contaminant mass discharge during a 19 month period following field application of the ZVI-Clay soil mixing remediation technology. Field data have been collected from a dense multilevel sampler network down-gradient of the source zone for calculation of the development in down-gradient mass discharge. A two-dimensional (2D) numerical groundwater model has been developed with the objective of improving the conceptual understanding of the mass discharge development and identifying the governing processes. Finally, the mass discharge reduction has been related to the source mass depletion presented in the companion paper (Fjordbøge et al., 2012) using an analytical power law model.

2. Materials and methods

2.1. Field investigations and remediation

Descriptions of the field site with its seven discrete tetrachloroethene (PCE) source zones and the source mass depletion by ZVI-Clay soil mixing (source zone V) are provided in the companion paper Fjordbøge et al. (2012). Prior to the remediation, the soil concentrations of the parent compound PCE were as high as 12,000 mg/kg, and separate phase PCE was extracted from the monitoring well in the central part of the source zone. This has resulted in heavy contamination of the upper secondary aquifer. Natural attenuation by anaerobic dechlorination was observed at the site (slow, electron donor-limited degradation). Specific degrading microorganisms (*Dehalococcoides* sp.) were detected in several monitoring wells, including a monitoring well around 5 m down-gradient of the source zone (KB17). Prior to the remediation the source zone mainly consisted of PCE (86%), and a smaller amount (7%) of trichloroethene (TCE). One year after the implementation of ZVI-Clay soil mixing over the full thickness of the upper secondary aquifer, these compounds were almost completely degraded with ethene as the main degradation product. The degradation in the source zone did not result in accumulation of cis-dichloroethene (cDCE), while minor amounts of vinyl chloride (VC) were produced at the up-gradient boundary of the source zone.

2.1.1. Monitoring network

The monitoring network for groundwater contaminants consisted of two types of wells. Eight nested monitoring wells with two screens each were placed in the source zone surroundings and dedicated to the monitoring of the remediation (Fig. 1). Four of the monitoring wells were placed 3–6 m down-gradient of the source zone (KB141–144), while the remaining four were placed around the mixed area: immediately down-gradient (DB4), 1.5 m north of the area (KB145), 1.5 m south of the area (KB107), and 2 m up-gradient (KB96). The nested wells were screened in the upper part of the upper secondary aquifer 2–3 m below ground surface (bgs), and in the lower part of the upper secondary aquifer 4–6 m bgs. The nested wells were installed in 15 cm (6") auger-drilled boreholes, and each well had a screen diameter of 63 mm. Additional wells used primarily for the site characterization (baseline) and measurement of the hydraulic head were also located in the surroundings of the source zone.

One multilevel sampler (MLS) was placed 8 m up-gradient of the source zone in order to monitor inflow concentrations to the area, while nine other MLSs (F1–F9) were placed in a transect perpendicular to the flow direction 3 m down-gradient of source zone V (Fig. 1). The installation and design of the MLSs were similar to that described by Rügge et al. (1999). The MLSs were installed by Geoprobe (5.4 cm or 2.125" OD) in a design that covered the entire contaminant plume with a control plane width of 16 m and a depth of 5 m (2–7 m bgs). The MLSs were placed with the largest sampling point density at the central 6 m of the transect; this was equivalent to the width of the source zone. The MLSs had a mutual horizontal distance of 1.5–3 m. Each MLS consisted of a PVC rod with 11 Teflon