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Source Zone Remediation by ZVI-Clay Soil-Mixing: Reduction of Tetrachloroethene Mass and Mass Discharge at a Danish DNAPL Site

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ABSTRACT

ZVI-Clay soil-mixing is a relatively new *in situ* remediation technology for remediation of chlorinated dense non-aqueous phase liquids (DNAPLs). The technology combines abiotic degradation (via zero-valent iron, ZVI, addition) and immobilization (via soil mixing and clay addition), whereby both contaminant mass and contaminant mass discharge can be reduced. The technology was tested at a Danish tetrachloroethene (PCE) site. The field sampling consisted of baseline measurements and a 19-month monitoring program (7 sampling campaigns) subsequent to the implementation of ZVI-Clay soil-mixing. The concentrations of chlorinated ethenes were monitored via soil sampling at the source zone and groundwater sampling at a down-gradient control plane. The results showed that within one year ZVI-Clay soil-mixing resulted in significant mass depletion of PCE (2-3 orders in magnitude) with ethene as the main degradation product. The down-gradient reduction of contaminant mass discharge was slower; after 19 months a mass discharge reduction of 76 % was obtained for the parent compound PCE, while the overall mass discharge reduction of chlorinated ethenes was 21 %.

INTRODUCTION

Chlorinated solvents have been widely used as industrial solvents. The presence of chlorinated solvent source zones in the subsurface poses a continuous threat to soil and groundwater quality at numerous sites worldwide. DNAPL in the subsurface poses a particularly challenging problem. To protect the soil and water resources from long-term deterioration, the development of *in situ* technologies suitable for remediation of DNAPL is warranted. An array of aggressive *in situ* remediation technologies currently exists. These technologies may be suitable under various site specific conditions; however, most of them are limited by heterogeneities in the subsurface and/or the risk of inadvertent DNAPL displacement during field application.

ZVI remediation technologies have proven effective in the remediation of various compounds and especially chlorinated aliphatic compounds (Gillham & O'Hannsin, 1994; Arnold & Roberts, 2000). Addition of ZVI through soil-mixing has been introduced as a new ZVI remediation technology (Bozzini et al., 2006; Wadley et al., 2005), which is being developed at Colorado State University (CSU). The ZVI-Clay soil-mixing technology provides a delivery mechanism that mechanically reduces subsurface heterogeneities (Fig. 1). The remediation technology ideally combines abiotic degradation (via ZVI addition) and immobilization (via soil-mixing and clay addition), whereby a great potential for both contaminant mass and contaminant mass discharge reduction is obtained.

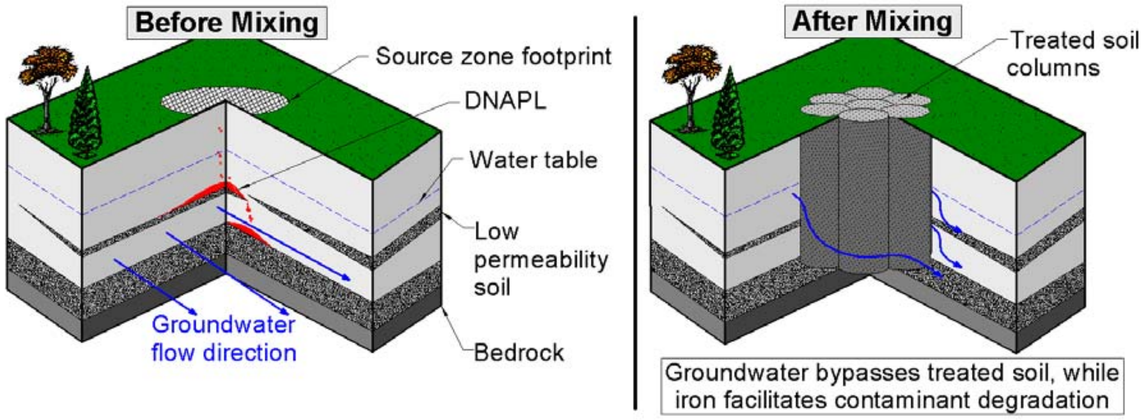

Fig. 1. Conceptual model of ZVI-Clay soil-mixing: (left) the heterogeneous subsurface before soil-mixing, and (right) the homogenized low-permeable subsurface after soil-mixing with bypassing groundwater (CSU, 2007)

Since 2007, different aspects of the ZVI-Clay technology have been investigated at a Danish site with a DNAPL source zone (Fjordbøge, 2011). The main objective of the presented study was to investigate the mass depletion at the DNAPL source zone and the following down-gradient response in the contaminant mass discharge.

MATERIALS AND METHODS

Site description

The field site was located at a former Danish metal processing factory (1968-83). During the period of operation significant amounts of PCE were released to the secondary aquifer, where several discrete PCE source zones have been characterized. One of these source zones was chosen for remediation with ZVI-Clay soil-mixing (Fig. 2).

The chosen source zone had an estimated mass of 360 kg PCE in the upper secondary aquifer (2-7 m bgs.) with soil concentrations ranging over several orders of magnitude (up to 12,000 mg/kg). In December 2008, ZVI-Clay soil-mixing was implemented at the small DNAPL source zone (around 200 m^3); approximately 1 % bentonite and 3 % microscale ZVI were added to the source zone.

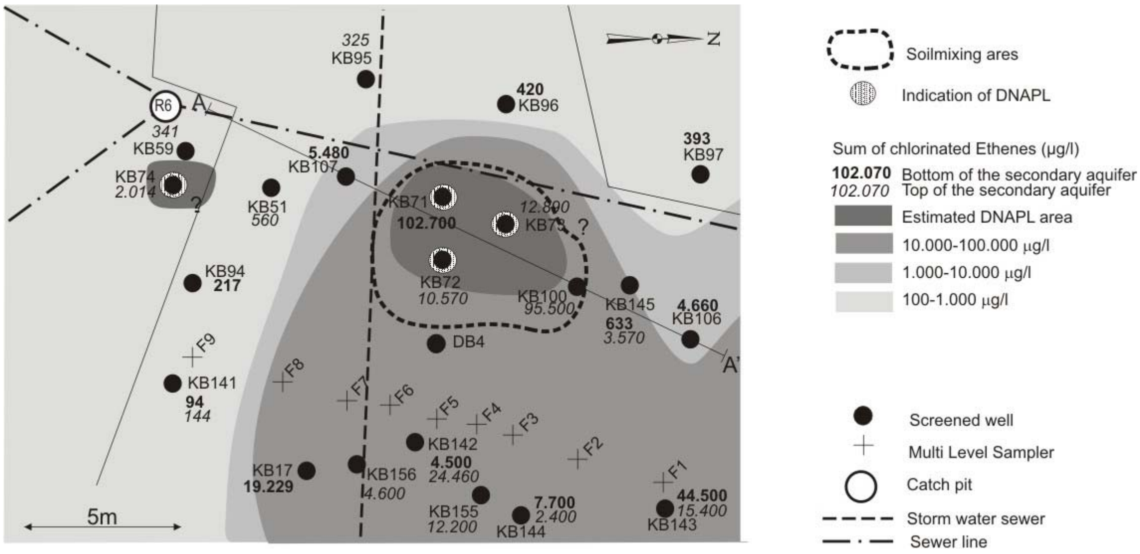

Fig. 2. Overview of the source zone area before ZVI-Clay soil-mixing incl. the location of the area that was later soil-mixed, the down-gradient multilevel samplers (MLSs) and several of the conventional screened wells in the surrounding area.

Field sampling

Field sampling at the source zone (soil samples) consisted of measurements taken immediately after the soil-mixing and during a 12-month monitoring program (5 sampling campaigns) following the implementation of ZVI-Clay soil-mixing. The samples were collected by a GeoProbe system and analyzed for chlorinated ethenes, total iron content and oxidation-reduction potential (ORP).

In November 2008, a control plane of 9 MLSs, covering the entire plume, was installed 3 m down-gradient. A single MLS was installed up-gradient to monitor any changes in the inflow concentrations. The MLSs in the control plane were placed with a mutual distance of 1.5-3 m (total width of 16 m) and screened at every 0.5 m (2-7 m bgs.). The field sampling down-gradient of the source zone (water samples) at the site consisted of baseline measurements and a 19-month monitoring program (7 sampling campaigns) following the implementation of ZVI-Clay soil-mixing. The concentrations of chlorinated ethenes were measured at all the well screens, the hydraulic conductivity was determined based on slug tests in the monitoring wells at the control plane and a pump test in the secondary aquifer, and the hydraulic gradient was determined based on the water table measurements in the surrounding area (13-17 wells) (Fjordbøge, 2011).

Mass discharge estimation

The mass discharge, M_D ($M\ T^{-1}$), was estimated based on (Troldborg et al., 2008):

$$M_D = \sum_{i=1}^{n} C_i\ A_i\ K_i\ \mathrm{d}h/\mathrm{d}l\ , \tag{1}$$

where the concentration, C_i ($M\ L^{-3}$), was measured, the area, A_i (L^2), was a rectangular cell defined by the half distance to adjacent sampling points in the vertical and horizontal direction, the saturated hydraulic conductivity, K_i ($L\ T^{-1}$), was based on the slug tests and the geology, and the hydraulic gradient, dh/dl (dimensionless), was attributed a constant value of 3 ‰ based on the water table measurements.

Numerical modeling

The collected field data were used for 2D numerical modeling (Comsol Multiphysics 4.0) of the solute transport of PCE in the sandy aquifer. The modeling was used to improve the conceptual understanding and to make long-term prediction of the contaminant mass discharge.

RESULTS AND DISCUSSION

Soil-mixing

The analysis of total iron confirmed an average iron enrichment of 3 % in the source zone. More efficient soil-mixing was achieved vertically compared to horizontally. The horizontal homogenization was limited, while the vertical homogenization was considerable for the iron content, the encountered geological layers, and the contaminants. As a result the addition of ZVI reduced the ORP significantly and established conditions favorable for abiotic reduction of the chlorinated solvents (Fjordbøge, 2011).

Contaminant mass depletion in the source zone

The favorable conditions for abiotic reduction of chlorinated solvents resulted in a significant mass reduction of PCE. PCE was continuously degraded during the monitoring period with a half-life around 2 months. Within one year the ZVI-Clay soil-mixing resulted in a significant mass depletion of PCE (2-3 orders of magnitude) with ethene as the main degradation product (β-elimination). More than 95 % of the collected soil samples were reduced below the remediation criterion of 5 mg/kg for PCE (Fjordbøge, 2011).

Contaminant mass discharge reduction down-gradient of the source zone

Initially PCE was the main groundwater contaminant with a mass discharge of 600 g/yr at the control plane 3 m down-gradient of the source zone. Over time the composition of the groundwater contaminants changed due to dechlorination in the area down-gradient of the source zone, and cis-DCE became the dominant contaminant. Within the 19-month monitoring period, the contaminant mass discharge of PCE was reduced 76 %, while the overall reduction of chlorinated ethenes was limited to 21 % due to the production of cis-DCE.

Also, the contaminant mass discharge of PCE changed from a more disperse contamination pattern at the control plane to a contamination pattern centered around seven MLS screens in the central part of the control plane, while being essentially removed in the rest of the cross-section of the plume (Fjordbøge, 2011).

Contaminant mass discharge modeling

Based on preliminary modeling the reduction of the contaminant mass discharge of the parent compound, PCE, was initially expected to be more extensive within the 19-months monitoring period (Jørgensen, 2008). Additional modeling was done to predict the long-term contaminant mass discharge and the factors affecting it.

The modeling identified 3-4 distinct temporal phases for the contaminant mass discharge i.e. stable baseline conditions, a rapid initial decline in the mass discharge, a potential temporary increase in the mass discharge, and a slower long-term mass discharge reduction. The initial decline in the contaminant mass discharge was primarily achieved through the changed hydraulic properties following soil-mixing, while the later changes were impacted by the changed concentration gradient at the boundaries of the soil-mixed source zone e.g. the changed accessibility of the contaminant and the rate of the mass depletion following ZVI addition (Fjordbøge, 2011).

Based on the modeling it was estimated that it would take 3-5 years to achieve a contaminant mass discharge reduction of 2-3 orders in magnitude.

CONCLUSION

The ZVI-Clay soil-mixing technology was efficient for source mass depletion in the presence of DNAPL. Within one year following the implementation of ZVI-Clay soil-mixing, removal efficiencies of around 2-3 orders of magnitude were generally achievable, at the source zone, without the formation of toxic chlorinated intermediates. The contaminant mass depletion was followed by a slower reduction of the down-gradient contaminant mass discharge of the parent compound. Chlorinated intermediates were formed in the plume, which reduced the overall removal efficiency of the chlorinated compounds.

As an *in situ* remediation technology, ZVI-Clay soil-mixing was found to be a viable alternative to other *in situ* remediation technologies, especially at sites were subsurface heterogeneities pose a problem.

ACKNOWLEDGMENTS

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