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Use of emulsified vegetable oil to support bioremediation of TCE DNAPL in soil columns

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ABSTRACT

The interaction between emulsified vegetable oil (EVO) and trichloroethylene (TCE) dense non-aqueous phase liquid (DNAPL) was observed using two soil columns and subsequent reductive dechlorination of TCE was monitored over a three year period. Dyed TCE DNAPL (~75 g) was emplaced in one column (DNAPL column), while the second was DNAPL-free (plume column). EVO was added to both columns and partitioning of the EVO into the TCE DNAPL was measured and quantified. TCE (1.9 mM) was added to the influent of the plume column to simulate conditions down gradient of a DNAPL source area and the columns were operated independently for more than one year, after which they were connected in series. Initially limited dechlorination of TCE to cDCE was observed in the DNAPL column, while the plume column supported complete reductive dechlorination of TCE to ethene. Upon connection and reamendment of the plume column with EVO, near saturation levels of TCE from the effluent of the DNAPL column were rapidly dechlorinated to c-DCE and VC in the plume column; however, this high rate dechlorination produced hydrochloric acid which overwhelmed the buffering capacity of the system and caused the pH to drop below 6.0. Dechlorination efficiency in the columns subsequently deteriorated, as measured by the chloride production and *Dehalococcoides* counts, but was restored by adding sodium bicarbonate buffer to the influent groundwater. Robust dechlorination was eventually observed in the DNAPL column, such that the TCE DNAPL was largely removed by the end of the study. Partitioning of the EVO into the DNAPL provided significant operational benefits to the remediation system both in terms of electron donor placement and longevity.

1. Introduction

Microcosm studies performed as a precursor to this study using soil and groundwater from a field site in the United Kingdom (UK) demonstrated that emulsified vegetable oil (EVO) was among the most effective electron donors in promoting complete reductive dechlorination of trichloroethylene (TCE) to ethene in microcosm bottles containing aqueous phase TCE concentrations up to 4.2 mM (550 mg/L) (Harkness et al., 2012). Due to its low aqueous solubility and structure containing long-chain fatty acid groups, the soybean oil in EVO is slowly fermented over time to produce hydrogen and volatile fatty acids, giving it significant operational advantages over soluble donors which must be added continuously or semi-continuously to maintain effectiveness (Harkness, 2000; Lalman and Bagley, 2000).

In addition, EVO belongs to a class of electron donors that have the potential to partition into the chlorinated solvent dense non-aqueous phase liquid (DNAPL) phase (Cápiro et al., 2011; Yang and McCarty, 2002). This property confers multiple advantages with respect to bioremediation. The soybean oil will be retained in the same location as the DNAPL phase rather than being transported out of the target remediation zone. Because a multi-component NAPL is now formed, the solvent concentration in the aqueous phase will

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be reduced based on Raoult's law, and with it toxic self-inhibition for the dechlorinating bacteria (Yang and McCarty, 2000a; Yu and Semprini, 2004). At the same time, high solvent concentrations in proximity to the DNAPL phase will continue to inhibit other bacteria that compete with the dechlorinators for hydrogen, ensuring the electron donor will be used more efficiently (Yang and McCarty, 1998). Finally, the soybean oil will eventually become available again as the DNAPL dissolves, providing an ongoing source of carbon and energy for the dechlorination process.

The column studies described herein were designed to achieve two objectives. The first was to understand how EVO transports through a real soil matrix and interacts with a residual TCE DNAPL phase. The use of EVO is complex and dynamic because EVO is an emulsion of soybean oil, surfactants, soluble substrate (lactate), and nutrients. The dilute emulsion phase is not stable in soil and will become trapped in the soil pore space and break over time, causing the soybean oil to be transferred from the emulsion onto the soil surfaces (AFCEE, 2007). Partition coefficients (log K_{vw}) for TCE between vegetable oils such as coconut and olive oil and groundwater have been measured and are somewhat less than that for octanol and water, but on the same order (Pu et al., 2008). Therefore aqueous phase TCE can partition into the soybean oil either inside the emulsion droplets or on the soil surface. As previously stated, the soybean oil can also partition into a chlorinated solvent DNAPL.

A second objective of the study was to observe the long-term impact of the EVO on TCE reductive dechlorination with and without the presence of DNAPL. This objective was achieved by operating two soil columns for more than 900 days. One column (DNAPL column) contained ~75 g of TCE DNAPL, the second column contained only soil (plume column). The columns were operated independently for approximately one year, then the plume column was connected in sequence after the DNAPL column and operated for an additional 600 days, until the majority of DNAPL was removed through dissolution and biodegradation.

Of particular interest here is the impact of pH on reductive dechlorination. Bioremediation remedies typically seek to maximize biodegradation rates, both to enhance the dissolution of the DNAPL phase to accelerate source removal and to produce complete transformation of daughter products to ethene (Seagren et al., 1993, 1994). Both the fermentation of electron donors and the reductive dechlorination of TCE and its daughter products generate acid (McCarty et al., 2007). If the acid production is significant enough it can overwhelm the natural buffering capacity of the soil system and cause the system pH to drop (McCarty et al., 2007; Robinson et al., 2009). These pH shifts have been observed in other degradation studies of PCE DNAPL (Adamson et al., 2003; Amos et al., 2009). Fermenting bacteria appear to operate most efficiently at a pH above neutral (Lee et al., 2002), while the performance of dechlorinating bacteria is optimum around pH 7.0 or above and known to decline as the pH approaches 6.0 (Middledorp et al., 1999; Zhuang and Pavlostathis, 1995). *Dehalococcoides* group (Dhc) bacteria, the only currently known bacteria capable of dechlorinating cDCE and VC to ethene, are particularly sensitive to pH, so that these latter dechlorination steps can be substantially impaired during pH excursions (Findlay et al., 2011). Maintenance of circum-neutral pH therefore becomes critical to producing maximum reductive dechlorination rates and achieving optimal remedy performance (Chu et al., 2004; Kouznetsova et al., 2010).

The studies presented here were performed as part of project SABRE, a public/private consortium of twelve companies, two government agencies, and three research institutions whose charter was to determine if enhanced anaerobic bioremediation can result in effective and quantifiable treatment of chlorinated solvent DNAPL source areas. The focus of this 4-year, $5.7 million dollar research and development project was a field site in the UK containing a DNAPL source area with groundwater concentrations ranging from 1140 to 8370 micromolar (μM) (150 to 1100 milligrams per liter (mg/L)) TCE. The results of the experiments were used to inform the design and operation of the SABRE field program, which used EVO to remediate an estimated 1000 kg of TCE DNAPL in a 30 m long × 4 m wide × 6 m deep test cell at the site.

2. Material and methods

2.1. Sample collection and processing

The soil used in this study was obtained from the field site in the UK. Subsurface soil samples were collected in acetate sleeves from the DNAPL source area using a direct push drilling rig. The acetate sleeves were capped and sealed immediately upon retrieval, packed in iced coolers and sent by courier to GE Global Research. Upon arrival, the soil was transferred from the sleeves to glass jars and stored under anaerobic conditions. The soil was sifted through 0.64 cm screens to remove any large rocks or debris, then mixed under anaerobic conditions to homogenize the contents. Approximately 50% of the material was too large to pass through the screens and was discarded. Additional soil samples were set aside for microbial analyses, acid titration testing, and solid phase total organic carbon (TOC) analysis.

2.2. Column construction and operation

The column experiments were run using two soil columns, one containing TCE DNAPL (DNAPL column) and one without DNAPL (plume column). The columns were glass chromatography columns (5.0 centimeter (cm) inside diameter (ID) × 60 cm length) fitted with Teflon endcaps (Fig. 1). The columns were fitted with five equally spaced glass sampling ports (1.0 cm ID) sealed with Teflon-coated butyl rubber stoppers to allow for groundwater sampling. Glass wool was used to keep soil from filling the sampling port extensions. The columns were covered with aluminum foil during operation to inhibit the growth of photosynthetic organisms. Synthetic groundwater was pumped into the bottom of each column using a FMI (Oyster Bay, NY) QG 6 positive displacement metering pump capable of producing flow rates in the range of 2–3 mL/h or less. The synthetic groundwater was pumped from opaque 3.4 L Tedlar™ bags held in Plexiglas holders, where the exterior surfaces of the bags were blanketed in nitrogen to reduce the levels of oxygen in the groundwater.

The composition of the synthetic groundwater was designed to approximate the chemistry of the groundwater found at the site (see Supplemental materials for recipe). Key