

LOW-VOLUME HYDROGEN BIOSPARGING IN AN EXPERIMENTAL CONTROLLED RELEASE SYSTEM

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ABSTRACT: In this SERDP-funded study, low-volume pulsed biosparging was examined as a means to effectively deliver hydrogen in situ. Two objectives of the study were to determine the efficacy of hydrogen for PCE reductive dechlorination in a controlled system and the effectiveness of bioaugmentation with a dechlorinating culture from Rice University. The experiments were conducted in an experimental controlled release system (ECRS), a covered sand-filled tank, which was used to simulate a contaminated aquifer. Dissolved PCE was circulated at 1.6 mg/L at a flow rate of 0.4 L/min (0.1 gpm). The tank was inoculated with a dechlorinating culture grown in a suspended growth reactor at Rice University. Hydrogen was typically sparged at 14 standard liters per min (0.45 scfm) for 1 minute as required.

Within 10 days of bioaugmentation, significant reductive dechlorination was observed. PCE removal rates ranged from 50 to 100%, with an average of 82%. The amount of PCE removed exceeded the amount of daughter products (i.e., trichloroethylene, cis-1,2-dichloroethylene (cDCE), vinyl chloride (VC), ethene) measured in the effluent. Approximately 2% of the added PCE was present as daughter products in the headspace, indicating that volatilization was not a major loss pathway. Microcosm data indicated that VC may also be degraded via anaerobic oxidation.

INTRODUCTION

Laboratory and field studies have shown that hydrogen is a key electron donor for stimulating the biological reductive dechlorination of chlorinated solvents (Carr and Hughes, 1998; Newell et al., 2000, 2001). Effective distribution of hydrogen in field applications is an ongoing challenge. One method that has the potential to effectively deliver hydrogen in contaminated groundwater is low-volume pulsed hydrogen biosparging (LVPB-H₂). Low gas volumes are used to minimize hydrogen breakthrough, while intermittent sparging is employed to minimize gas usage and increase mixing. Pulsed biosparging has the potential to more effectively deliver hydrogen than continuous sparging (Rutherford and Johnson, 1996). One concern regarding direct hydrogen addition is that high hydrogen concentrations may favor bacterial populations such as sulfate reducers and methanogens, which could compete with the dechlorinating population for hydrogen. In this work, we demonstrate high PCE removals, at high hydrogen saturations.

Objectives. Two objectives of this work were:

- Determine the effectiveness of high hydrogen saturations for the reductive dechlorination of PCE and its daughter products in a controlled system and

- Determine how effective bioaugmentation of a dechlorinating culture would be for degrading PCE.

EXPERIMENTAL EQUIPMENT AND METHODS

Experimental Controlled Release System. The Experimental Controlled Release System (ECRS) is a 1428-L (5400-gallon) rectangular tank (5.5 m (18 feet) long, 2.1 m (7 feet) wide, and 1.8 m (6 feet) tall) equipped with 60 sampling ports, 2 sparge wells, pumps, and ancillary water tanks. The 1428 L tank served to simulate a contaminated aquifer. It was filled with clean, fine commercial grade masonry sand with a mean hydraulic conductivity of 0.1 cm/s and a fraction of organic carbon (foc) of 0.001.

A saturated solution of PCE was metered into the influent to achieve a concentration of 1.6 mg/L or 9.7 μ M. The PCE-laden water was pumped to the front end of the tank and distributed within the tank using three interconnected well screens. Water was passed through the tank at approximately 0.4 L/min (0.1 gpm), corresponding to a hydraulic retention time of approximately 11 days. The effluent was treated with activated carbon to remove chlorinated constituents and ethene prior to being circulated to the head of the tank. Acetate was added periodically at concentrations between 20 and 30 mg/L.

Hydrogen gas was metered into the tank using a rotameter, and the flow was controlled with a solenoid valve on a timer. Hydrogen was sparged into a well located 6 ft from the head of the tank. The hydrogen was sparged at 14 standard L/min (0.45 scfm) for 1 minute as required (typically five times per week). Hydrogen saturations of as high as 9.6% were achieved.

Bacterial Culture and Bioaugmentation. The bacterial consortium used for bioaugmentation was cultured at Rice University in a 113-L (30-gallon) bioreactor. The reactor was inoculated with a stock of rapidly dechlorinating microorganisms that had been fed methanol and PCE for a period of eight years (Carr and Hughes, 1998). The system was operated as a fed-batch reactor for 6 months with routine additions of PCE and lactate.

After turning the ECRS tank anaerobic, it was sparged with hydrogen each day for 1 minute at 14 standard L/min. (0.45 scfm) to provide ample electron donor. The Rice University culture was added to six locations near the primary sparge point. In total, 8 liters of culture at a VSS of 38 mg/L, or 4.3 grams of bacteria, were added to the tank.

Analytical Methods. Chlorinated ethenes, ethene, and methane concentrations in aqueous samples were determined using headspace analysis. Samples (100 μ L) were injected directly into a gas chromatograph (GC) (Hewlett-Packard 5890) equipped with a flame ionization detector (FID) and a packed column containing 60/80 Carbopack B/1% SP-1000 (Supelco). The operating parameters of the GC have been previously described by Carr and Hughes (1998).

Gas samples from the ECRS tank headspace were collected using summa canisters and sent to Research Triangle Park Laboratory for analysis. The headspace gas was analyzed for chlorinated ethenes by GC/MS using Method TO-14A, and ethene, ethane, and methane were analyzed by GC/FID using EPA Modified Method 18.

RESULTS AND DISCUSSION

VOC Effluent Data. To achieve a simulated dissolved PCE groundwater plume, saturated PCE was metered into the influent water to achieve a mean concentration of 9.7 μM . Within 45 days after bioaugmentation, PCE concentrations were not detected in the effluent as shown in Figure 1. cDCE was the first daughter product to show up in the effluent, only 9 days after bioaugmentation (Figure 2). TCE, vinyl chloride and ethene were detectable by the 17th day post-bioaugmentation. Evidence of complete dechlorination was observed as early as 17 days after bioaugmentation. Therefore, the bioaugmented culture rapidly degraded PCE and its daughter products, with a very short lag period, and continued to dechlorinate for the duration of the experiment.

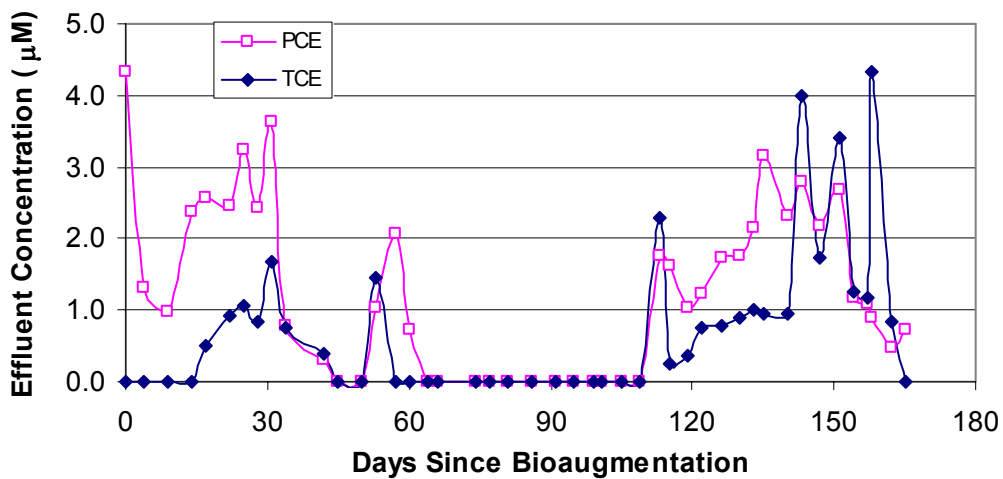


FIGURE 1. Concentration of PCE and TCE in ECRS effluent.

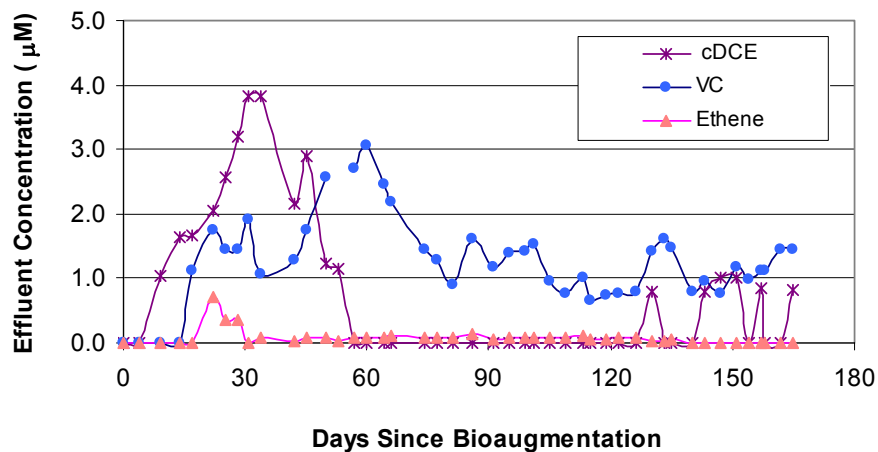


FIGURE 2. Concentration of cDCE, VC, and ethene in ECRS effluent.

No PCE or TCE was found in the effluent from day 64 through 113, representing 100% removal of PCE and TCE (Figure 1). After 115 days, the concentration of PCE and TCE began to rise in the effluent. It was hypothesized that the system was either electron donor or carbon limited; so the amount of acetate added to the influent was increased to 30 mg/L and the amount of hydrogen injected was increased to 45 standard L/min (1.6 scfm). Acetate addition provided a source of carbon for growth, as it is not used by the dechlorinating culture as an electron donor for reductive dechlorination (J. Hughes, personal communication). By the end of the experiment, PCE and TCE concentrations had once again declined to less than 1 μM .

cDCE demonstrated a different trend than PCE and TCE (Figure 2). It was produced very early (within 14 days) from the bioaugmentation and began to rise rapidly over the first 30 days. From day 30 to day 60, cDCE concentrations declined, presumably due to production of vinyl chloride (which increased over the same time period). No cDCE was measured in the effluent, from day 60 to day 120. Then, over the last month, small concentrations (less than 1 μM) were observed in the effluent.

For the bulk of the experiment, vinyl chloride concentrations in the effluent remained relatively constant (Figure 2). Sixty days after bioaugmentation, vinyl chloride concentrations reached a maximum of 3 μM and then declined to 1-1.5 μM for the remainder of the experiment. Despite high conversion of PCE, TCE, and cDCE from day 64 to day 113, vinyl chloride did not accumulate. However, the ethene data indicates that vinyl chloride was not significantly reduced to ethene. Ethene was present in the effluent from days 22 to 135 at low concentrations and then was not detectable for the remainder of the experiment.

Between days 64 and 105, the composition of the effluent was more than 90% vinyl chloride (Figure 3), but the actual concentration of vinyl chloride was only between 1 and 3 μM , significantly less than the mean influent PCE concentration of 9.7 μM . These results suggested that other mechanisms in addition to reductive dechlorination were responsible for the low concentrations of vinyl chloride during periods of high conversion of PCE, TCE, and cDCE.

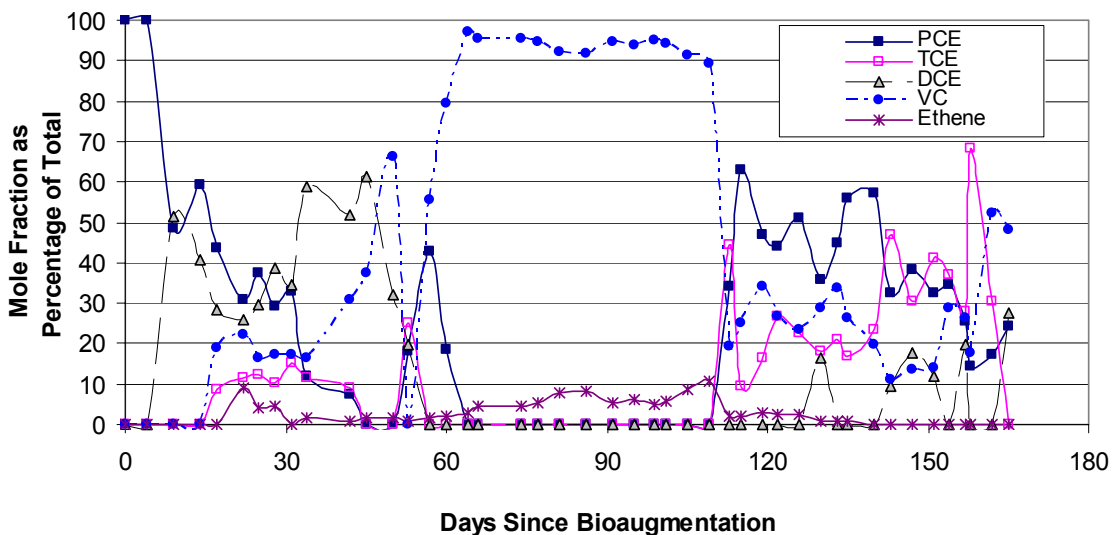


FIGURE 3. ECRS effluent composition over course of the experiment.

Microcosm Studies. Because not all the degraded PCE could be accounted for by chlorinated ethene daughter products and ethene and iron reduction was occurring within the ECRS tank (data not shown), microcosm experiments were conducted to determine if vinyl chloride was being degraded via anaerobic oxidation coupled to ferric iron reduction. A sample of the culture from the ECRS tank and a deionized water control were each amended with 2 mM of ferric iron and spiked with 0.01 mM of VC under anaerobic conditions. Over 300 hours, vinyl chloride in the microcosm with ECRS culture declined 32% while the vinyl chloride in the deionized water control with no bacteria decreased by 18%, as shown in Figure 4. Despite some volatile losses in the control, vinyl chloride anaerobic oxidation appeared to be a possible biodegradation mechanism.

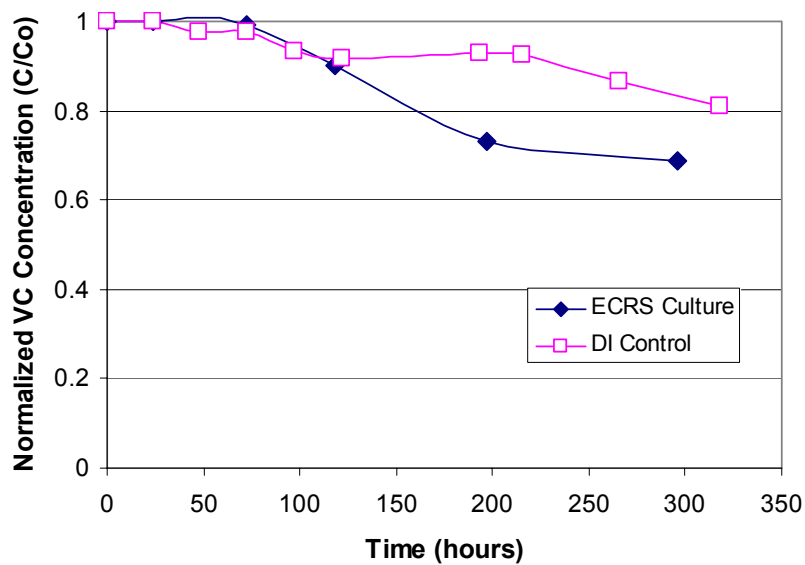


FIGURE 4. Microcosm studies to examine VC degradation under ferric iron reducing conditions.

Quantification of Volatilization Losses. To quantify volatile losses of chlorinated constituents, ethene, and ethane during the hydrogen sparge, samples of the ECRS tank headspace were taken within 30 minutes of the sparge over the course of the experiment. As shown in Table 1, volatilization of PCE and its reductive dechlorination daughter products were not a significant loss mechanism. The mean amount of daughter products lost in the effluent as a percentage of the amount of PCE entering the ECRS was 2.4%. Volatilization was minimal due to the low-volume pulsed sparge regime, which aimed to inject gas without significant breakthrough.

TABLE 1. Volatile losses from the ECRS.

Constituent	Mean Amt. Leaving Tank (mmoles/day)	% of PCE Entering Tank
PCE	0.030	0.6
TCE	0.014	0.3
cDCE	0.003	0.06
VC	0.048	0.9
Ethene + Ethane	0.029	0.5
TOTAL	0.124	2.4%

System Performance. The system performance was monitored over the course of the six-month experiment as summarized in Table 2. The total PCE removed was 82%, and 78% was biotransformed. Fifty-three percent of the total chlorinated constituents were removed, with 46% being biodegraded. These performance data represent good removals, considering the effluent was located only 12 feet downgradient of the sparge well. Higher removal efficiencies would be expected at distances further downgradient due to other biodegradation processes such as anaerobic oxidation. Although there was a decline in performance, due in part to carbon limitations, this is unlikely to be a factor in the field where there is usually a continuous background source of natural organic carbon.

Seventy-three percent mass balance closure was obtained using the chlorinated constituents and ethene concentration in the effluent and off-gas. Some of the mass not captured may be due to the production of carbon dioxide through vinyl chloride oxidation under iron reducing conditions.

TABLE 2. ECRS performance data.

Constituent	Moles In	Moles Out (Water)	% Removed	Moles Out (Off-Gas)	Moles Sorbed	% Biotransformed
PCE	0.776	0.139	82.1	0.003	0.027	78.3
TCE	0.000	0.051	-6.6	0.002	0.012	-8.3
cDCE	0.000	0.076	-9.8	0.003	0.000	-9.9
VC	0.000	0.102	-13.1	0.006	0.001	-14.0
Ethene	0.000	0.007	-0.9	0.003	0.000	-1.4
Total	0.776	0.368	52.6	0.011	0.040	46.0
Chlorinated						% Closure
Chlorine	3.10	0.96		0.035	0.143	72.5

Methane Generation. Throughout the course of the experiment, methane concentrations increased gradually from 0 mg/L to as high as 1.6 mg/L. Despite increasing levels of methane, methane concentration had no impact on the extent of PCE removal, as seen in Figure 5. Therefore, although methanogens can consume hydrogen, methanogenesis did not inhibit PCE reductive dechlorination as the concentrations increased.

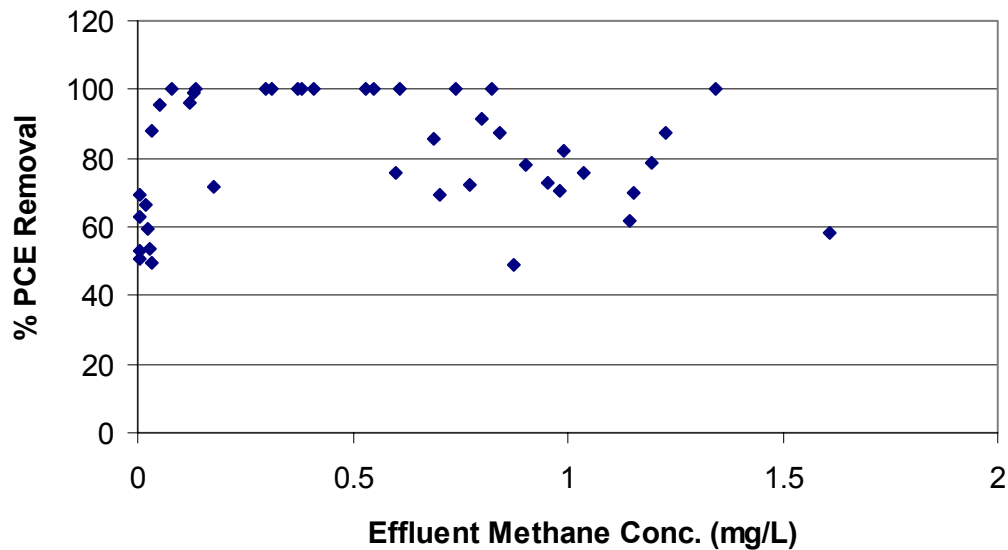


FIGURE 5. Effect of methane concentration on PCE removal.

CONCLUSIONS

1. Bioaugmentation with the Rice University culture was successful since evidence of complete reductive dechlorination was observed within 17 days and the bacteria remained viable over the course of the 6-month experiment.
2. Good PCE removals (82%) were achieved over a short distance (18 ft) using only one sparge well. A mass balance closure of 73% was achieved.
3. Only 2% of the chlorinated constituents volatilized during sparging, indicating that volatilization was not a major loss mechanism for PCE or its reductive dechlorination products.
4. Vinyl chloride did not accumulate to levels approaching the mean influent PCE concentration of 9.7 μM . Some vinyl chloride may have been lost via other degradation processes such as anaerobic oxidation.
5. Methanogenesis did not prevent reductive dechlorination even though high hydrogen saturations were present in the ECRS tank.

ACKNOWLEDGMENTS

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