

RESULTS FROM TWO DIRECT HYDROGEN DELIVERY FIELD TESTS FOR ENHANCED DECHLORINATION

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ABSTRACT: Direct hydrogen addition, wherein hydrogen is delivered without the use of fermentation substrates or carbon sources is an in-situ bioremediation technology for chlorinated solvent plumes that is currently under development. A multi-site project to field test the applicability and feasibility of direct hydrogen addition has been initiated by the Technology Transfer Division at the Air Force Center for Environmental Excellence (AFCEE).

Results from a **pull-push-pull treatability test** devised by one of the authors (Haas) conducted at Offutt AFB in Nebraska in Nov. 1998 showed > 99% reduction of the cis-DCE in a 900 L test volume over the 41 hour test period (0.43 to < 0.005 mg/L) and > 99% decrease in the amended hydrogen.

Results from the four-month sampling event from a planned 18-month **low-volume pulsed biosparging test** at Cape Canaveral Air Station Florida also showed apparent biological dechlorination in a 48 x 90 ft test zone located 15-20 ft below the water table in a sandy aquifer. Analysis of the gas tracers after one week indicated extensive biological utilization of hydrogen. At the four month interval, data from 14 sampling points in the test area indicated significant reductions in TCE (e.g., from 48 mg/L to < 0.005 mg/L in one well) and cis-DCE concentrations (e.g., 140 mg/L to 4 mg/L in one well) compared to the 2 points in the nitrogen control area. No excessive methane production was observed in the hydrogen delivery zone.

INTRODUCTION

Hydrogen is now widely recognized as a key electron donor required for the biologically-mediated dechlorination of chlorinated compounds (e.g., see Wiedemeier et al. 1999). In this process, hydrogen acts as an *electron donor* and halogenated compounds such as chlorinated solvents act as *electron acceptors*, becoming reduced in the reductive dechlorination process.

While much of the early research has focused on indirect hydrogen addition of via the delivery of fermentation substrates such as methanol, toluene, lactate, benzoate, etc. and the subsequent fermentation of these substrates to form hydrogen, it is also possible to deliver the hydrogen directly without the

fermentation step. Direct delivery methods that have been proposed by Hughes, Newell, and Fisher (1997) include circulation of groundwater containing dissolved hydrogen, placement of chemical agents that release dissolved hydrogen, electrolysis of water with subsurface electrodes, use of colloidal gas aphanes (foams), and low-volume pulsed biosparging.

Work performed by Carr and Hughes (1998) showed no microbiological constraints on the direct addition of hydrogen (i.e., no restrictions on the dechlorinating bacteria due to competition effects with other bacteria). Therefore they concluded that selection of the most appropriate method of hydrogen delivery (e.g., addition of fermentation substrates vs. direct delivery) is based on factors such as cost and the relative efficiency of hydrogen distribution within the treatment area (Carr and Hughes, 1998).

Several direct hydrogen delivery field tests, one with introduction of water amended with dissolved hydrogen, and one with low-volume pulsed biosparging of hydrogen have been completed under the AFCEE test program. Two of these projects are described below.

TEST 1: PULL-PUSH-PULL TREATABILITY TEST

Test Procedure. A pull-push-pull treatability test was performed at the Fire Protection Training Area 3 (FPTA 3) site at Offutt AFB, Nebraska. Across the majority of the site, groundwater occurs at 8 to 10 ft below ground surface (BGS) within a sand unit. Starting concentrations of key contaminants at the site were less than 1 mg/L of cis-DCE and less than 1 mg/L of total BTEX. As described in Fisher et al., 1999, the hydrogen pull-push-pull treatability test consists of the following steps:

- 1) *Initial Groundwater Extraction ("pull")*: Extraction of a known quantity of groundwater (e.g., 750 L) from within the test area through an existing monitoring well.
- 2) *Amendment Addition*: Addition of known quantities of hydrogen and various volatile and non-volatile tracers (e.g., bromide, helium, sulfur-hexafluoride (SF₆)) to the extracted groundwater, followed by thorough mixing to create a homogeneous test solution.
- 3) *Initial Sampling*: Collection of a representative test solution sample which is analyzed for chlorinated organic compounds, hydrogen, tracers, and other constituents of interest (e.g., oxygen, nitrate, sulfate, etc.).
- 4) *Re-Injection of Groundwater Test Solution*: Pulse injection ("push") of amended groundwater into the saturated zone through the same monitoring well used for groundwater extraction.
- 5) *Final Groundwater Extraction*: Extraction ("pull") of the test solution/groundwater mixture from the test well following a contact/reaction period (typically 24 to 48 hr). Sampling is conducted during the extraction.

- 6) *Final Sampling:* Collection of a final representative test solution sample which is again analyzed for chlorinated organic compounds, hydrogen, tracers, and other constituents of interest.

Test Results. cis-1,2-DCE concentrations dropped by more than 99% (0.43 to < 0.005 mg/L) over the course of the 41-hour test, while much lower reductions in Total BTEX was observed (34% reduction). Due to the expected similar volatilization and adsorption behavior of DCE and BTEX (based on similar Henry's Law and organic carbon partitioning coefficients), the observed substantial loss of DCE does not appear to be fully accounted for by these physical mechanisms, and a biological loss is indicated. Tracer recovery results indicate a minimum 39% mass loss of hydrogen to biological consumption over the course of the 41-hour treatability test at FPTA 3 (0.012 mg/L hydrogen consumed). Although a biological reduction of all of the cis-1,2-DCE is indicated, it could not be confirmed by observed changes in vinyl chloride or ethene concentrations.

TEST 1: LOW-VOLUME PULSED BIOSPARGING TEST

Test Procedure. Cape Canaveral Air Station is located on a barrier island along the Atlantic coast of Florida, separated from the Florida mainland by the Banana River. Launch Complex 15 is one of a series of rocket launching facilities located along the easternmost edge of the Base, adjoining the Atlantic Ocean. The near-surface soil/aquifer material at Launch Complex 15 consists of silica sand with some shell, and little clay or organic matter. The sand unit is continuous from the surface to the maximum explored depth of approximately 70 ft below ground surface (BGS), with some silt and clay lenses at depth. Groundwater is typically encountered at 6 - 7 feet below ground surface. The observed potentiometric surface is very flat, with less than 0.1 ft of head difference over the 90 ft.

The hydrogen biosparging pilot test system at Launch Complex 15 utilizes a 4-sparge point, 20-monitoring point well network in a 48 x 90 ft area as shown in Figure 1. Three hydrogen sparge points, spaced 12 ft apart, and 16 monitoring wells located within the treatment zone are being used to determine the rate and extent of chlorinated solvent degradation over the test period. The fourth sparge point and an additional 4 monitoring wells are being used as a nitrogen sparge control for purposes of assessing chlorinated solvent losses occurring through volatilization as a result of sparging activities.

In addition to the four rows of upgradient/downgradient monitoring wells, additional monitoring points in the form of six multi-level saturated zone samplers and three multi-level vadose zone samplers were installed immediately adjacent to the hydrogen sparge points. These samplers allow for the collection of data concerning the distribution of sparged gases within the treatment zone.

Hydrogen biosparging equipment at Launch Complex 15 consists of 5 T-size compressed gas cylinders (256 scf each) linked to a common manifold, an adjustable pressure regulator, an automatic timer-activated solenoid valve, direct reading flow gages, and stainless steel tubing connecting the gas cylinders to the three hydrogen sparge wells. A parallel nitrogen sparging system utilizes a single T-size compressed gas cylinder connected to a single sparge well. System power is provided by a 12-volt gel-cell battery equipped with a solar-powered recharging circuit. The initial gas mixture consisted of 48% hydrogen, 48% helium, and 2% SF₆ so that all compounds would have a theoretical equilibrium concentration with the water of about 0.8 mg/L.

The sparging system operates on a pulse cycle controlled by a timer such that gas is sparged in a burst of a set duration, occurring at a specified frequency. Injection pressures are approximately 20 psig, sufficient to overcome hydrostatic pressure within the sparge wells (approx. 9 psig). Approximately 130 scf of a 49% hydrogen, 49% helium, and 2% SF₆ gas mixture was pulsed into each of the three sparge points (located on 12 ft centers) on the first day of sampling (2/7/99). Note that no breakthrough of hydrogen gas to the surface was detected during this initial sparging event (vadose zone thickness: 5 ft). After the first day, smaller 1-minute “maintenance” pulses consisting of 15-20 scf of research grade hydrogen gas were added to each sparge point once per day. Recently the system has been reconfigured to delivery one large pulse of hydrogen once a week.

Test Results. Results from the four-month sampling event of the planned 18-month low-volume pulsed biosparging test at Cape Canaveral Air Station showed hydrogen transfer, hydrogen consumption, and apparent biological dechlorination in the test zone located 15-20 ft below the water table in a sandy aquifer.

After 1 week, hydrogen and tracer concentrations were measured in the multi-level samplers located in the sparging row (see Figure 2). The maximum observed hydrogen concentration was 0.47 mg/L, or a little over half of the equilibrium hydrogen concentration of 0.8 mg/L for the initial injection gas (comprised of 48% hydrogen, 48% helium, and 2% SF₆). Overall significant reductions in hydrogen concentration were observed horizontally and vertically away from the gas sparge points. Comparison with the helium and SF₆ showed a larger distribution of these tracers, indicating biological consumption of the injected hydrogen. Overall each sparge point appeared to deliver hydrogen concentrations in about a 5 ft radius away from the sparge point (10 ft diameter).

At the four month interval, data from 14 sampling points in the test area indicated significant reductions in TCE (see Table 1 and Figure 3) and cis-DCE concentrations (see Table 1 and Figure 3) compared to the 2 points in the nitrogen control area (see Table 2). No excessive methane production was observed in the hydrogen delivery zone (see Table 1).

TABLE 1. Results from Cape Canaveral Low-Volume Pulsed Hydrogen Field Test: Hydrogen Sparge Test Section.

Constituent	Geometric Mean of 6 CLOSE Sampling Pts in H ₂ Test Zone (3-6 ft horizontally from sparge points)				Geo. Mean of 8 MIDDLE Sampling Pts in H ₂ Test Zone (15 ft horizontally from sparge pts)		
	2/7/99 (mg/L)	2/13/99 (mg/L)	6/23/99 (mg/L)	4 Month Change (mg/L)	2/7/99 (mg/L)	6/23/99 (mg/L)	4 Month Change (mg/L)
TCE	14.1	8.1	0.5	- 13.6	15.9	10.8	- 5.1
cis-DCE	237.	239.	88.	- 149.	193.	155.	- 38.
Vinyl Chl.	39.	22.	21.	- 18.	32.	34.	+ 2.
Ethene	2.6	1.8	1.5	- 1.1	3.2	2.8	- 0.4
Methane	0.50	0.23	0.07	- 0.43	0.77	0.55	- 0.22

TABLE 2. Results from Cape Canaveral Low-Volume Pulsed Hydrogen Field Test: Nitrogen Sparge Control Section.

Constituent	Geo. Mean of 2 MIDDLE Sampling Pts in N ₂ Control (15 ft horiz. from sparge pt)		
	2/7/99 (mg/L)	6/23/99 (mg/L)	4 Month Change (mg/L)
TCE	0.55	0.39	- 0.17
cis-DCE	50.	45.	- 5.
Vinyl Chl.	24.	31.	+ 7.
Ethene	3.8	4.9	+ 1.1
Methane	2.0	3.2	+ 1.2

CONCLUSIONS

Two field tests of direct hydrogen delivery showed reductions in chlorinated solvent concentrations and consumption of hydrogen. In addition, a push-pull-push test showed conservation of benzene compared to consumption of cis-DCE, indicating that biological processes were responsible for the removal of cis-DCE rather than physical processes. Reductions in TCE and cis-DCE in a low-volume pulsed biosparging test were higher in the hydrogen test zone compared to a nitrogen control zone.

Additional pilot tests using injection water amended with dissolved hydrogen are now being planned. The low-volume pulsed biosparging system is still being operated, with sampling events planned for Feb. 2000 (one year of operation) and August 2000 (eighteen months of operation).

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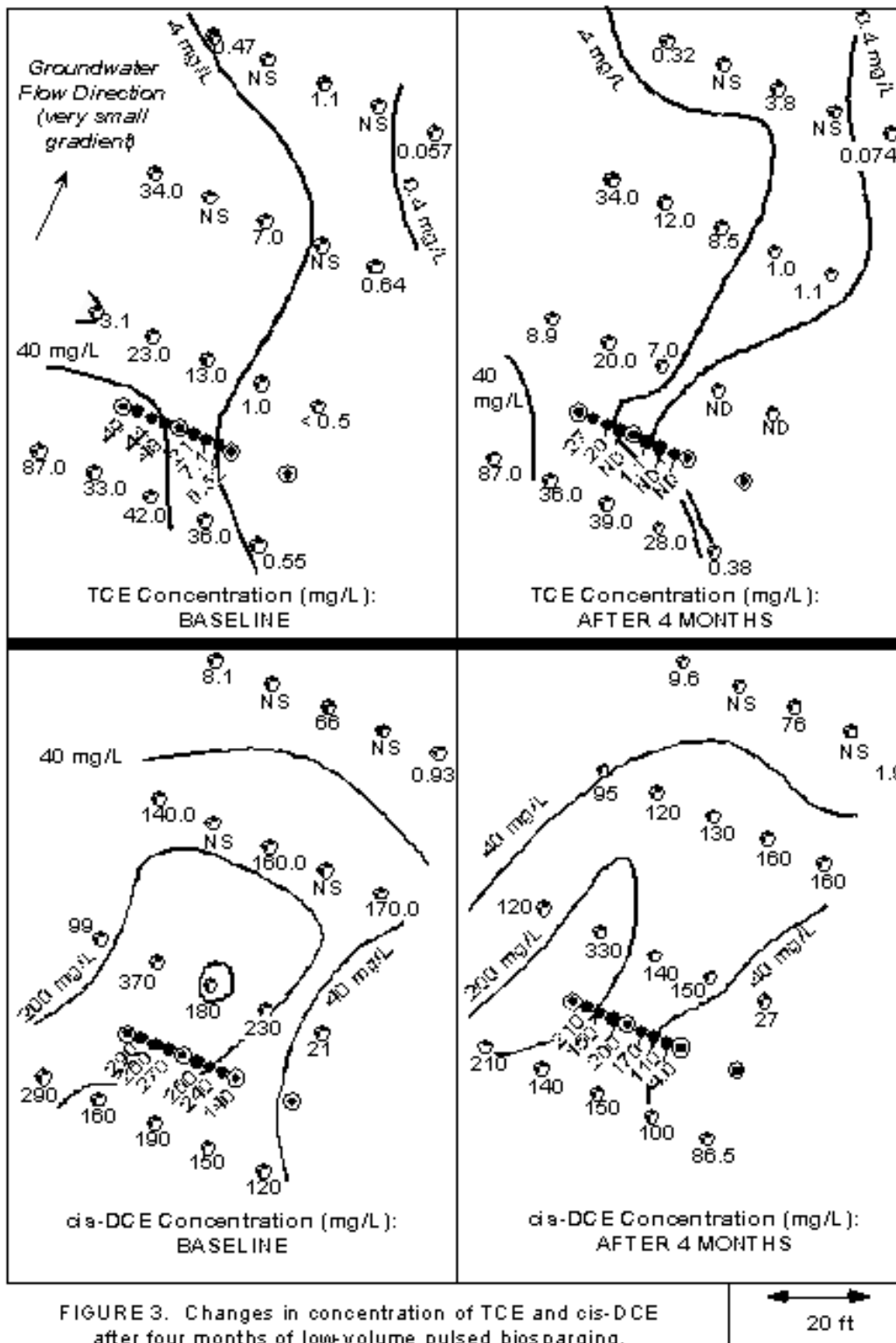


FIGURE 3. Changes in concentration of TCE and cis-DCE after four months of low-volume pulsed biosparging.