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Field Demonstration of DNAPL Dehalogenation

Using Emulsified Zero-Valent Iron

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ABSTRACT. This paper describes the results of the first field-scale demonstration conducted to evaluate the performance of nano-scale emulsified zero-valent iron (EZVI) injected into the saturated zone to enhance *in situ* dehalogenation of dense, non-aqueous phase liquids (DNAPLs) containing trichloroethene (TCE). EZVI is an innovative and emerging remediation technology. EZVI is a surfactant-stabilized, biodegradable emulsion that forms emulsion droplets consisting of an oil-liquid membrane surrounding zero-valent iron (ZVI) particles in water. EZVI was injected over a five day period into eight wells in a demonstration test area within a larger DNAPL source area at NASA's Launch Complex 34 (LC34) using a pressure pulse injection method. Soil and groundwater samples were collected before and after treatment and analyzed for volatile organic compounds (VOCs) to evaluate the changes in VOC mass, concentration and mass flux. Significant reductions in TCE soil concentrations (>80%) were observed at four of the six soil sampling locations within 90 days of EZVI injection. Somewhat lower reductions were observed at the other two soil sampling locations where visual observations suggest that most of the EZVI migrated up above the target treatment depth. Significant reductions in TCE groundwater concentrations (57 to 100%) were observed at all depths targeted with EZVI. Groundwater samples from the treatment area also showed significant increases in the concentrations of cis-1,2-dichloroethene (cDCE), vinyl chloride (VC) and ethene. The decrease in concentrations of TCE in soil and groundwater samples following treatment with EZVI is believed to be due to abiotic degradation associated with the ZVI as well as biodegradation enhanced by the presence of the oil and surfactant in the EZVI emulsion.

KEY WORDS. EZVI, emulsified zero-valent iron, nano-scale iron, DNAPL

Introduction

Chlorinated solvents are present in groundwater at an overwhelming number of contaminated sites. The United States Environmental Protection Agency (EPA) estimates that of the current 8,336 Department of Defense (DoD) sites requiring cleanup, 5,418 sites (documented and suspected cases) have been impacted by chlorinated solvents (1). A significant number of these sites have VOCs present as free-phase dense non-aqueous phase liquids (DNAPLs) that will act as a long-term source of VOCs to groundwater. An expert panel on DNAPL remediation appointed by US EPA reported recently that "the total number of DNAPL impacted sites in the U.S. could range from 15,000 to 25,000" (2). Due to the slow dissolution of solvents from residual or pooled DNAPL source areas, conventional treatment technologies such as pump and treat serve solely as containment technologies and require long operational periods (i.e., decades or longer) to satisfy the need for protection of human health and the environment, incurring high operation and maintenance costs over that period (2).

Significant attention has been devoted in the past few years to research and field-applications of source treatment technologies, as they have the potential to lower the overall cost and time required for remediation of contaminated aquifers. There is a need for technologies that can effectively treat DNAPL source zones in saturated media, destroy significant mass and reduce the flux of chemicals from the source zones. Recently, GeoSyntec, the University of Central Florida (UCF) and NASA Kennedy Space Center conducted a demonstration to evaluate the performance of an emulsified zero-valent iron (EZVI) technology when applied to DNAPL

contaminants in the saturated zone. The results of the EZVI demonstration were also evaluated under the EPA's Superfund Innovative Technology Evaluation (SITE) Program. Battelle Memorial Institute (Battelle) evaluated the performance of the EZVI technology under contract to the SITE Program.

Technology Description. Significant laboratory and field research has demonstrated that zero-valent metal particulates will degrade dissolved chlorinated solvents such as tetrachloroethene (PCE) and TCE to ethene (3, 4, 5). Permeable reactive barriers (PRBs) using ZVI are passive and require no energy; however, they still rely on DNAPL dissolution and transport of dissolved chlorinated solvents to the PRB for treatment, and as a result, PRBs do little to reduce the clean-up time and subsequent long-term monitoring costs for sites with DNAPL. The EZVI technology using nano-scale or micro-scale iron was developed to address this limitation associated with the conventional use of ZVI. It is hypothesized that EZVI can be used to enhance the destruction of chlorinated DNAPL in source zones by creating increased contact between the DNAPL and the nano-scale ZVI and by providing vegetable oil to enhance biological activity.

EZVI is composed of food-grade surfactant, biodegradable vegetable oil, and water, which form emulsion particles (or droplets) that contain the ZVI particles (either nano- or micro-scale iron may be used) in water surrounded by an oil-liquid membrane. For the demonstration, Sunlight brand corn oil, a nonionic surfactant sorbitan triolate (Span 85), and nano-scale iron purchased from Toda America (RNIP, Toda's iron product) were combined into the following mass ratios: 44.3% water; 37.2% oil; 1.5% surfactant; and 17.0 % iron.

Figure 1 shows a schematic and a magnified image of an emulsion droplet. Since the exterior oil membrane of the emulsion particles has hydrophobic properties similar to that of DNAPL, the emulsion is miscible with the DNAPL

Figure 2 illustrates the properties of EZVI in contact with DNAPL in small-scale laboratory tests. In Figure 2A, TCE has been dyed red with Sudan IV and sits as a separate DNAPL phase in contact with water. In Figure 2B, powdered micro-scale ZVI has been added to an identical mixture of TCE and water and all three components remain as separate layers, with the TCE on the bottom, ZVI above it and the water on top. In the third vial, Figure 2C, EZVI has been added to a vial containing Sudan IV-dyed TCE and water. The TCE DNAPL and EZVI are now miscible providing increased contact between the TCE DNAPL and the ZVI within the droplet's interior. The black coating that is evident above the water in Figure 2C is the EZVI smeared onto the glass; above the water level the EZVI is glass-wetting.

Encapsulating the ZVI in a hydrophobic membrane protects the nano-scale iron from other groundwater constituents, such as inorganic materials, that might otherwise use up some of the reducing capacity of the nano-scale iron while allowing organic constituents (TCE and other ethenes) to diffuse through the liquid membrane and contact the ZVI. This potentially reduces the mass of EZVI required for treatment relative to unprotected ZVI. It is hypothesized that the EZVI will combine directly with the target contaminants (DNAPL) until the oil membrane is dissolved and consumed by biological activity.

Laboratory experiments conducted at UCF (6) demonstrated that DNAPL constituents such as TCE pass through the oil-liquid membrane of the emulsion and degrade in the presence of ZVI

particles in the interior of the emulsion droplet, resulting in the formation of non-chlorinated hydrocarbon products (e.g., acetylene, ethene, and ethane). Laboratory testing performed at UCF concluded that the rate constants for TCE degradation are in the same order of magnitude for both EZVI and ZVI alone (7). The degradation of TCE in the presence of the ZVI is believed to occur via some combination of reductive dechlorination and β-elimination (8). The hypothesized mechanism for the interaction of the DNAPL constituents and the ZVI particles within the droplets is diffusion from the oil/DNAPL layer (DNAPL miscible with the oil) into the aqueous center of the emulsion droplet. It is hypothesized that the final by-products (non-chlorinated hydrocarbons) from the dehalogenation reaction are driven by the increase in concentration inside the emulsion droplet to diffuse out of the emulsion into the surrounding aqueous phase.

EZVI has an average viscosity of 1942 centipoise (cp) and a specific gravity of approximately 1.1 (measured using a pycnometer). The oil-liquid membrane allows the EZVI to be miscible with DNAPL contamination in the subsurface. The primary application of the technology is treatment of DNAPL source-zones but it is also capable of treating dissolved phase contaminants in the vicinity of DNAPL. The reduction in concentration of dissolved phase contaminants in the vicinity of the DNAPL will also enhance the rate of mass dissolution from the DNAPL.

In addition to the abiotic degradation associated with the ZVI, the injection of EZVI containing vegetable oil and surfactant will result in enhanced biodegradation of dissolved chlorinated ethenes because the vegetable oil and surfactant act as electron donors to promote anaerobic biodegradation processes. Abiotic degradation resulting from the ZVI in the EZVI was shown to be a very fast process in laboratory studies conducted at UCF (6). If insufficient ZVI is present

to completely degrade the TCE to ethene then the vegetable oil and surfactant will act as a long-term electron donor source for anaerobes to continue the degradation process should they exist at the Site (9).

Test Site Description. Launch Complex 34 at Cape Canaveral Air Force Station (LC34), Florida, USA, was used as a launch site for Saturn rockets from 1960 to 1968. Historical records suggest that rocket engines were cleaned on the launch pad with chlorinated organic solvents, including TCE. During cleaning operations the solvents either evaporated, infiltrated directly into the subsurface, or migrated as runoff into surface drainage features at the site. LC34 was abandoned as a launch facility in 1968 and since that time much of the site has become overgrown with vegetation. DNAPL is present in the subsurface at the site as a result of historical releases from Site operations. The DNAPL consists primarily of TCE, although cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC) also are present in groundwater as a result of intrinsic TCE biodegradation processes (10).

The technology demonstration was conducted in a small area (15 ft by 9.5 ft) underneath the Engineering Support Building (ESB) in an extensive zone of known DNAPL contamination. The soil cores collected before EZVI injection were used to determine the presence of TCE DNAPL in the demonstration area. The concentrations of TCE in groundwater within the demonstration test area at the Site prior to injection of the EZVI ranged up to the solubility of TCE.

A surficial aquifer and a semi-confined aquifer beneath a clay unit comprise the major water bearing units at LC34 and are illustrated in Figure 3. The demonstration was conducted in the

surficial aquifer, which extends from the water table to approximately 45 feet below ground surface (ft bgs). The surficial aquifer is sub-classified as having an upper sand unit (USU), a middle fine-grained unit (MFGU), and a lower sand unit (LSU) (10). The USU is composed of medium to coarse-grained sand and crushed shells and extends from ground surface to approximately 18-25 ft bgs. The MFGU is composed of gray, fine-grained silty/clayey sand and extends from approximately 18 ft bgs to 30 ft bgs. The EZVI demonstration was conducted in the USU and in the upper few feet of the MFGU. The water table varies between 3 and 7 ft bgs. During the EZVI pilot test the groundwater elevation varied from approximately 3.85 to 4.0 ft above mean sea level (ft msl) and there was little change over the duration of the test. The natural gradient at the site is relatively flat with horizontal gradients ranging from 0.00009 to 0.0007 ft/ft (11).

Objectives. The primary objective of the demonstration test was to estimate the changes in total TCE mass and TCE DNAPL mass in the target unit as well as the change in TCE flux to groundwater. Additional objectives were to: a) evaluate changes in aquifer quality due to the EZVI treatment; b) evaluate the fate of TCE due to the EZVI treatment; and c) verify EZVI technology operation requirements. The total TCE mass includes both dissolved phase and free-phase TCE present in the targeted aquifer unit. DNAPL can be inferred when the soil concentrations exceed the theoretical maximum chemical mass that can be adsorbed to soil, dissolved in the water within the soil sample, and volatilized in the soil gas. In this paper, TCE DNAPL refers to free-phase TCE only and for the purpose of this evaluation is defined by the threshold TCE concentration (C_t) of 300 mg/Kg in soil, above which it is assumed that DNAPL is present, calculated based on assuming equilibrium partitioning (12):

$$C_t = \frac{C_{water}(K_d \rho_b + n)}{\rho_b}$$

Where:

C_t = maximum TCE concentration in the dissolved and adsorbed phases (mg/Kg)

C_{water} = TCE solubility (mg/L) = 1,100 (13)

ρ_b = bulk density of soil (g/cm^3) = 1.59 (10)

n = porosity (unitless) = 0.33 (assumed)

K_d = partitioning coefficient of TCE in soil [(mg/Kg)/(mg/L)],
equal to ($f_{oc} \cdot K_{oc}$) = 0.0652

f_{oc} = fraction organic carbon (unitless) = 0.0005 (assumed from measured range; 10)

K_{oc} = organic carbon partition coefficient for TCE [(mg/Kg)/(mg/L)] = 126 (13).

Changes in TCE mass flux to groundwater were estimated based on measurement of TCE concentrations in groundwater sampled from the multilevel wells located up-gradient and down-gradient of the demonstration test area.

Methods

The interfacial surface tension was tested in the laboratory using a Fisher-brand Surface Tensiometer with a Fisher-brand platinum-iridium ring measuring 6.000 cm in circumference. The interfacial surface tension between EZVI and water, TCE and water, and EZVI, TCE, and water were each measured. Multiple trials for each materials combination were performed, with repeatable results. Measurements were taken by placing an aliquot of liquid in a 100 mL beaker

so that the ring was submerged at least 0.25 inches below the surface with no contact to the beaker.

Pre-Demonstration Monitoring and Set Up. Six continuous soil core samples were collected prior to the recirculation of groundwater or the injection of EZVI. The soil samples collected before and after the demonstration were sampled using a stainless steel sleeve driven into the subsurface by a Vibra-Push drill rig. After the sleeve had been driven the required depth, it was brought to the surface and one quarter of the sample (approximately 150 to 200 g of wet soil) was sliced from the core and placed into a pre-weighed 500 ml polyethylene container containing methanol. To acquire this sample, each four foot soil core was divided in half length-wise and then each two foot section was quartered, again length-wise so that a representative sample from the entire core depth was extracted. The remaining soil sample was examined and characterized for lithology. The methanol-preserved soil samples were stored at 4°C until the extraction procedure was performed. Soil samples were preserved and extracted on site using modified method EPA 5035. To extract the VOCs from the samples, the soil/methanol bottles were weighed then placed on an orbital shaker table and agitated for a minimum of 30 minutes at 90 rotations per minute (rpm). The containers were then reweighed to ensure no methanol loss and the sediment was allowed to settle for 15 minutes. The sample containers were placed in a floor-mounted centrifuge and centrifuged for 10 minutes at 3,000 rpm. After removal from the centrifuge, the methanol extract was decanted into 20-mL glass volatile organic analysis (VOA) vials using 10–ml disposable pipettes and shipped on ice to the laboratory for analysis. Samples were analyzed for VOCs using method EPA 8260 at an off-site laboratory (14). Figure 4

illustrates the location of the soil cores collected and their relationship to other monitoring and injection points in the demonstration test area.

Groundwater samples were collected using inertial lift pumps (Waterra pumps) from the mid point of the screened interval. Prior to collection of the samples directly into preserved 40-mL VOA vials, the wells were purged until field-measured parameters stabilized (pH, dissolved oxygen, ORP, and specific conductance measured using either a Horiba® U-22 instrument (Horiba Instruments) or a YSI 556 multi-probe system (YSI Environmental, Inc.)),. Samples were stored at 4°C until shipped on ice to the off site laboratory for analysis.

Slug tests were performed on well PA-23 within the EZVI plot before and after the demonstrations to assess effects on aquifer quality caused by the EZVI. The slug test consisted of placing a pressure transducer and 1.5 inch-diameter by 5 ft long PVC slug into the well. After the water level reached equilibrium, the slug was quickly removed. Removal of the slug created approximately 1.5 ft of change in the water level within the well. Water level recovery was then monitored for at least 10 min using a TROLL® pressure transducer/data logger. The tests were repeated three times to ensure repeatable results. The recovery rates of the water levels were analyzed with the Bouwer (15) and Bouwer and Rice (16) methods for slug tests in unconfined aquifers with partially penetrating wells (14).

A groundwater control system was designed and installed to create a closed-loop recirculation cell and forced gradient conditions across the target treatment zone that would allow for a comparison of the flux to groundwater from the DNAPL source zone before and after treatment with the EZVI. A series of four multilevel monitoring wells (EML-1, EML-2, EML-3 and EML-

4) with five separate sample intervals and one fully screened well (PA-23) were installed in the pilot test area to provide groundwater chemistry data to evaluate the changes in concentrations and mass flux before and after EZVI injection. A set of groundwater samples was collected from each of the 21 groundwater monitoring points to determine baseline concentrations and mass flux. The groundwater recirculation system was operated at one gallon per minute (gpm) for three weeks prior to collecting the base line samples. Samples were collected semi-weekly from the extraction wells during groundwater recirculation to determine when quasi steady-state concentrations of TCE had been attained. Additional monitoring wells (PA-24 and PA-25) were installed at three separate depth intervals (shallow, intermediate and deep, corresponding to the Site lithologic units) outside the demonstration test area to monitor for potential changes in groundwater concentrations following the application of the EZVI technology. The groundwater recirculation system was shut off prior to injection of the EZVI.

EZVI Injection. The EZVI mixture used in the demonstration consisted of: 44.3% water, 37.2% oil, 1.5% surfactant and 17.0 % iron by weight. A range of iron contents for the EZVI were evaluated in the laboratory and a high iron loading was used for this first field-scale demonstration to allow treatment using a single EZVI injection. The nano-scale iron was purchased from Toda America, Inc., and consisted of nano-scale iron particles with dimensions of approximately 100 to 200 nanometers. The components of the EZVI were blended at the site using a Scott, Top-mount Turbo industrial emulsifying unit sized for a 55 gallon drum six weeks prior to injection. Each drum was filled approximately three quarters full with EZVI then a nitrogen purge was initiated across the available headspace. The lid was promptly closed as the nitrogen was shut off to minimize oxygen exposure to the EZVI prior to injection.

The EZVI was injected into eight separate 3-inch diameter wells in the demonstration test area (Figure 4) at two injection intervals per well (16 to 20.5 ft bgs and 20.5 to 24 ft bgs) using an injection method called pressure pulse technology (PPT). The PPT injection tool consists of a perforated injection pipe between two removable three foot long inflatable packers. For injection into the lower zone, the bottom packer was removed and the top packer was placed from 17.5 to 20.5 ft bgs and inflated to isolate the 20.5 to 24 ft bgs zone. Both bottom and top packers were used to inject into the 16 to 20.5 ft bgs interval and were set from 20.5 to 23.5 ft bgs for the bottom packer and from 13 to 16 ft bgs for the upper packer. PPT applies large-amplitude pulses of pressure to porous media, causing "instantaneous" dilation of the pore throats in the porous media, thus increasing fluid flow and minimizing the "fingering" effect that occurs when a fluid is injected into a saturated media (17).

The volumes of EZVI injected in each well and at each depth interval were adjusted based on the distribution of the VOCs as measured in the pre-demonstration soil cores and are presented in Table 1. Approximately 670 gallons of EZVI were injected into an area 15 feet by 9.5 feet over a 10 ft depth interval. During the injection of the EZVI, additional water was added to the injection points to enhance the distribution of EZVI into the formation. The additional water used for this purpose was obtained from monitoring well PA-23 located in the center of the demonstration area. EZVI was injected in August of 2002 over a five day period.

Post Demonstration Monitoring. Approximately two months after the injection of EZVI (October 2002), a set of four interim soil cores were obtained for visual confirmation that EZVI had been distributed to the target depth zone and to provide an initial assessment of the changes

in VOC concentrations is soil. Soil samples were collected and analyzed following the same procedures used for the pre-demonstration soil samples. Approximately three months after the injection of EZVI (November 2002), a set of six post-demonstration soil cores were obtained and soil samples collected and analyzed following the same procedures used for the pre-demonstration (pre-demo) soil samples. Figure 4 shows the locations of all soil cores and the injection and monitoring wells.

Five months after the injection of EZVI (January 2003) the groundwater recirculation system was turned back on and operated for a period of three weeks to allow for collection of groundwater samples to be compared with the groundwater samples collected prior to injection of EZVI. A set of 21 groundwater-monitoring points were sampled to evaluate changes in concentrations and mass flux. These groundwater samples are referred to as the post-demonstration (post-demo) samples. In addition, groundwater samples were collected 19 months after injection of EZVI (December 2003 and March 2004) to evaluate the "long-term" impacts of the treatment on VOC concentrations in groundwater.

Results and Discussion

Measurement of Interfacial Tension. The interfacial surface tension was tested in the laboratory and no significant change in interfacial tension between the DNAPL and water once the DNAPL was exposed to EZVI was measured. The interfacial surface tensions between EZVI and water, TCE and water, and EZVI, TCE, and water were each measured. Average values for the interface of a TCE and water system measured 33.5 dynes/cm. The average value for the system of EZVI and water was 40.0 dynes/cm, while that for the system of TCE, water, and

EZVI measured at 37.5 dynes/cm. EZVI is designed to be miscible with DNAPL due to its hydrophobic nature, and although there is a small amount of surfactant in the emulsion, no downward movement of the DNAPL was observed in any of the laboratory scale flow through cells or column tests performed (6).

Results of Analysis of Soil Samples. Table 2 presents the TCE concentrations measured in the soil samples from borings from the treated interval (16 to 24 feet bgs) as well as intervals below and above the target treatment interval. The sets of soil sampling locations (e.g., SB-3, SB-203, and SB-303) were taken from locations within approximately two feet of each other for the pre (SB-3), interim (SB-203) and post-demonstration (SB-303) and are intended to represent soil conditions in the same general area.

The soil samples which contained visual evidence of the presence of EZVI are shown as shaded in Table 2. Natural geologic material at the site consists of light colored sand and shell fragments, and therefore, the black colored EZVI is easily discernable from the natural material. Additionally, soil samples containing EZVI were examined under a microscope to verify emulsion droplet integrity within the subsurface. It is apparent, particularly in the vicinity of SB-3 and SB-8, that the EZVI when injected using PPT has a tendency to migrate up from the injection depth interval to more shallow intervals. It is believed that this upward migration of the EZVI in these sampling locations resulted in less effective degradation of TCE in the target treatment intervals at these two locations.

Table 2 presents the average TCE concentrations in soil samples in the target treatment interval for each of the soil cores as well as the percent reduction in the average concentrations following

treatment. It should be noted that although a direct comparison of the concentrations of each pre-, interim-, and post-demonstration core set is made, they are from the same general location only and not from the exact same spatial location. Significant reductions in TCE concentrations (> 80%) were observed at all soil boring locations with the exception of SB-3 and SB-8 where visual observations suggest that most, if not all of the EZVI migrated up above the target treatment depth. The SB-3 soil core results may indicate some mobilization of DNAPL downward within the demonstration test area since the concentrations of TCE at the 22 to 24 ft bgs samples increase from approximately 250 mg/kg in the pre-demonstration cores to 495 mg/kg one month after injection and then to 4,500 mg/kg three months after injection. However, one month post injection results show only a slight increase in concentration, suggesting that the variability in the DNAPL distribution prior to injection (i.e., the pre-demonstration core did not intersect the high DNAPL concentrations at this depth) may account for the observed concentration increase rather than mobilization due to injection of EZVI. One of the difficulties in using a set of soil cores to evaluate the performance of a DNAPL remediation technology is that DNAPL distribution in the subsurface is very complicated and although care may be taken to position the pre- and post-demonstration cores as close together as possible, the DNAPL distribution may vary significantly in the subsurface, making direct comparison of the pre- and post-demonstration results difficult to interpret. As a result of the potential difficulty in evaluating the performance of the technology with only the soil cores, groundwater concentrations and mass flux results were also used to evaluate the EZVI performance (discussed below).

To evaluate the overall effectiveness of the technology, the total TCE and TCE DNAPL mass in soil was estimated before and after treatment using a linear interpolation method and geo-statistical kriging. Kriging is a statistical interpolation method for analyzing spatially variable data. It was used in this study to obtain a global estimate of the TCE concentration (and hence, the mass) across the region of interest, (the EZVI demonstration test plot). Based on the spatial coordinates, the test plot was defined as a volume of 14.92 ft long x 9.46 ft wide x 20 ft deep. The software (GSLIB) and the methodology used for the kriging are described by Deutsch and Journel (18). The kriging approach included two primary analysis steps:

- Estimating and modeling spatial correlations in the available monitoring data using a semivariogram analysis.
- Using the resulting semivariogram model and the available monitoring data to interpolate TCE values at unsampled locations and calculate the statistical standard error associated with each estimated value.

This standard error was then used to calculate confidence bounds or confidence intervals for the global average TCE concentration within the test plot. The pre-demonstration data set consisted of 81 TCE measurements and the post-demonstration data set consisted of 104 TCE measurements. The level of significance of the statistical test was 80%.

The statistical results for linear interpolation and kriging are presented in Tables 3 and 4 respectively. Initial mass estimates by contouring estimated a total TCE mass in the USU of 17.8 kg and a TCE DNAPL mass of 3.8 kg. The total TCE pre-demonstration mass estimates using the geostatistical kriging method with an 80% confidence interval was 28 kg (10-46 kg

upper and lower bounds). Analysis of the data using linear interpolation suggests that the reduction in total TCE and TCE DNAPL following treatment with the EZVI was approximately 85%. Analysis of the data by kriging suggests that treatment reduced the total TCE mass by an average of 58%.

As shown in Tables 3 and 4, decreases in the TCE mass in the MFGU, below the treatment zone, were also observed. These decreases are believed to be in part due to the increase in biological activity in the area due to the addition of the EZVI.

Results of Analysis of Groundwater Samples. Table 5 presents the results of analysis of TCE in groundwater samples collected from the multilevel transect wells of the downgradient end of the treatment area and monitoring well PA-23 in the center of the treatment area (see Figure 4 for location). Significant reductions in TCE concentrations (i.e., 57% to 100%) were observed at all depths targeted with EZVI (16 to 24 feet bgs). The average reduction in concentration for the downgradient transect (E-ML-1 and E-ML-2) was 68% and the mass flux measured for this multilevel well transect decreased by approximately 56% from 19.2 mmoles/day/ft^2 to 8.5 mmoles/day/ft^2 over a period of 6 months. Groundwater samples from these wells also showed significant increases in the concentrations of cDCE, VC and ethene. The presence of cDCE and VC are likely attributable to biological reductive dechlorination of TCE, and the observed concentrations of these degradation products suggests that biodegradation accounts for a significant percentage of the decrease in TCE concentrations and DNAPL observed at the site. This is different from the results observed in the sterile laboratory

experiments where optimal mixing and contact of the EZVI with the DNAPL promoted rapid and complete degradation of TCE and the only measured end product was ethene.

Table 6 shows the results of analysis of TCE, cDCE, and VC in monitoring wells located outside the perimeter of the treatment area (see Figure 4 for locations). No significant increases in concentrations of TCE (greater than a factor of 2) were observed in the PA-24 wells and in the shallow and intermediate PA-25 wells. However, PA-25D had an order of magnitude increase in TCE concentration from 3 to 53 mg/L showing the potential for some redistribution of chemicals from the demonstration test area into the deeper treatment interval. Overall, the results suggest that the decreases in TCE observed in the demonstration test area are due primarily to destruction within the demonstration test area and not simply pushing VOC out of the area. In addition, soil data indicate that there is no increasing trend in TCE concentrations in the LSU.

Chloride concentrations in groundwater samples from PA-23 increased from 200 mg/L to as much as 294 mg/L, following treatment with EZVI which supports the dehalogenation of TCE. The complete dehalogenation of 1.23 mg/L of TCE will produce 1 mg/L of chloride. Based on the results seen at the site, complete dechlorination may not be occurring: however, the increase in chloride concentration of 94 mg/L suggests that some degree of dechlorination of TCE is occurring.

Nineteen months after injection (March 2004), a series of additional groundwater samples were collected and analyzed for TCE and its degradation products. The results of these analysis are presented in Table 5 and show that significant additional reductions in TCE occurred after the initial set of pre-demo groundwater samples were collected. It should be noted that the

"long-term" data was collected using a slightly different method then the "pre-demo" and "post-demo" data because the groundwater recirculation system was not operated prior to collection of the long-term samples. The molar concentrations of TCE, cDCE, VC and ethene in selected monitoring wells in the downgradient transect and PA-23 are presented in Figure 5. The results show reductions in the concentrations of cDCE in the long-term samples (EML1-4) and some samples show slightly increasing concentrations of VC relative to the initial post-demo samples (EML1-4 and EML2-4).

The long-term sample from EML2-4 (the bottom of the treatment zone in monitoring well EML2) shows significant increases in concentrations of cDCE and VC in the long-term samples that werenot observed in other monitoring points. This monitoring point is slightly downgradient of SB-8 where visual observations suggest that the EZVI migrated up from the target treatment zone and had the highest residual concentration of TCE following treatment with EZVI (i.e., in the post-demo sample with 300 mg/L). The increasing concentrations of cDCE and VC at this depth interval are believed to be the result of biodegradation of TCE outside the zone which received EZVI resulting in partial dechlorination of the TCE.

Ethene concentrations were measured in groundwater post-demonstration samples and in the long-term sample from monitoring well PA-23 located in the center of the demonstration test area. Ethene was observed in the post-demo samples from all monitoring locations and the long-term sample from PA-23 showed concentrations of ethene continuing to increase over time suggesting that degradation is still occurring between 5 and 19 months after injection of the EZVI.

Results indicate that even though EZVI was poorly distributed during its first field-scale injection, significant reductions in groundwater TCE concentrations (57% to 100%) were still observed at all depths targeted with EZVI within 5 months. The average reduction in groundwater concentration for this transect (E-ML-1 and E-ML-2) is 68%. Further decreases in TCE concentrations were observed in long-term groundwater samples collected 19 months after the injection of the EZVI. The data suggest that a significant portion of the loss of TCE may be due to other degradation mechanisms such as biodegradation enhanced by the presence of the oil and surfactant in the EZVI emulsion.

Consistent groundwater pH levels were also observed within the demonstration test area. Typical granular ZVI treatment walls shift pH up to the range of 9 to 11 (19), however with EZVI, it is hypothesized that the corrosion of the ZVI occurs within the individual emulsion droplets and the pH shift within the aquifer is minimal. The pH in shallow wells within the plot increased from an average of 6.5 before the demonstration to an average of 6.8 after the demonstration. A peak pH level of 7.2 was recorded.

There was no substantial change in the observed hydraulic conductivity following EZVI treatment, as shown by slug tests conducted at PA-23, which averaged 43 ft/day (0.015 cm/sec) and 38.2 ft/day (0.013 cm/sec) before and after treatment, respectively. An order-of-magnitude decrease in the hydraulic conductivity would be indictative of a substantial change in permeability. These results indicate that potential impacts such as the formation of iron oxides from the oxidation of EZVI or biofouling due to the presence of the oil and surfactant minimally impact the hydraulic conductivity of the aquifer.

Application Issues. The data from the field-scale demonstration of EZVI at LC34 demonstrated that significant quantities of TCE DNAPL could be degraded using the technology but that there were outstanding questions about how to obtain a more uniform distribution of EZVI around the injection points, and questions regarding the relative contributions of the abiotic and biological mechanisms to the degradation of TCE. Based on post-demonstration soil core samples, EZVI appears to have migrated up from the injection interval in some locations during its injection using PPT, was not evenly distributed within the target treatment area, and did not travel as far as expected from each of the injection points. In addition, there was a notable increase in the concentrations of intermediate products of sequential dechlorination (i.e., cDCE and VC). Lab studies using EZVI suggested that the degradation of TCE by EZVI produces very few degradation product intermediates when performed in a sterile environment (6). The average molar concentrations of cDCE and VC in groundwater samples accounted for 50% of the decrease in TCE concentrations suggesting that for this demonstration, a significant portion of the loss of TCE is due to other degradation mechanisms such as biodegradation enhanced by the presence of the oil and surfactant in the EZVI emulsion. Injection of EZVI in the field was complicated by many factors including injection into a heterogeneous formation, contact between the EZVI and DNAPL, natural degradation of the EZVI components promoting enhanced biodegradation of the TCE and formation of degradation byproducts. Therefore injection methodologies and relative contributions of abiotic and biological degradation need to be better understood for future use of the technology.

In an effort to address the questions associated with controlling subsurface injection, another field test was initiated in January of 2004 that focused on improving the EZVI delivery

mechanism (20). Four injection technologies were tested including: a) pneumatic fracturing, b) hydraulic fracturing, c) pressure pulsing, and d) direct injection. Four separate vendors were each given 100 gallons of EZVI made with nano-scale iron and directed to inject the material in an open field near the LC34 demonstration site between 16 and 19 feet bgs. The test objective was to control the depth interval into which the EZVI was injected and attempt to achieve the largest possible radius of influence. Pneumatic injection and direct push emerged as the most promising technologies, allowing for controlled injections without loss of EZVI above or below the targeted region. Prior to full-scale deployment, we recommend that the planned injection method be tested to confirm that it does not damage the emulsion droplets during the injection process.

Planned future work with EZVI includes another field-scale demonstration of EZVI funded by the DoD Environmental Security Technology Certification Program (ESTCP). The project will evaluate through laboratory microcosms, the proportion of the chlorinated solvent mass destruction that is occurring due to abiotic degradation versus the proportion that is due to the enhanced biodegradation that is occurring as a result of the addition of electron donor in the EZVI. Many of the unresolved issues with the application and performance of EZVI, including injection issues, DNAPL mobilization potential, and biodegradation will also be evaluated during this follow-on study.

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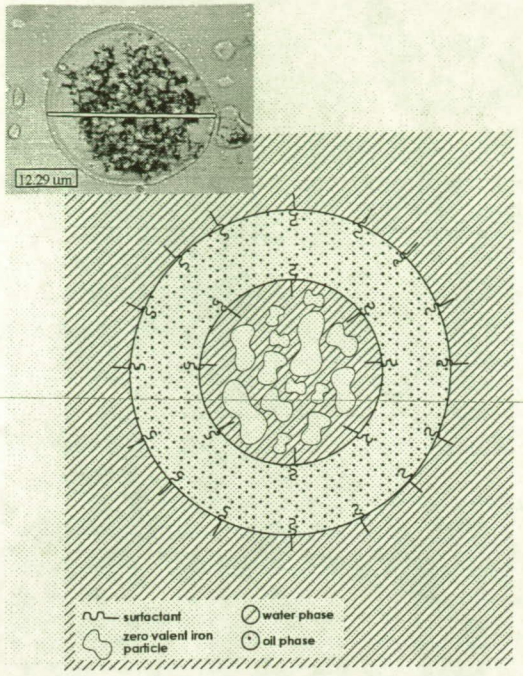
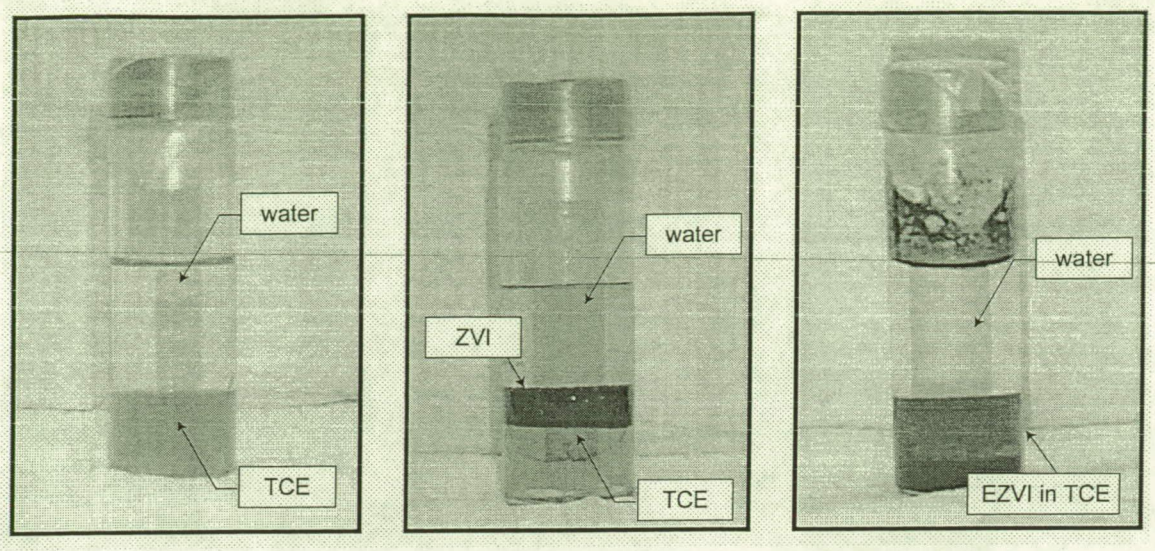


FIGURE 1. Schematic and photograph of EZVI droplet showing the oil-liquid membrane surrounding particles of ZVI in water.



A B C

FIGURE 2. Properties of ZVI and EZVI in Contact with DNAPL. TCE dyed with Sudan IV in water (A) shows two distinct phases. TCE dyed with Sudan IV in water mixed with powdered micro-scale ZVI (B) shows distinct phases and ZVI separate from the TCE DNAPL phase (1.0 g iron). TCE dyed with Sudan IV in water and EZVI (C) shows a distinct water phase and a single DNAPL phase with the TCE and the EZVI combined. EZVI mass % used in pictures: 15.7 % iron, 26.3 % water, 56.6 % oil and 1.3 % surfactant.

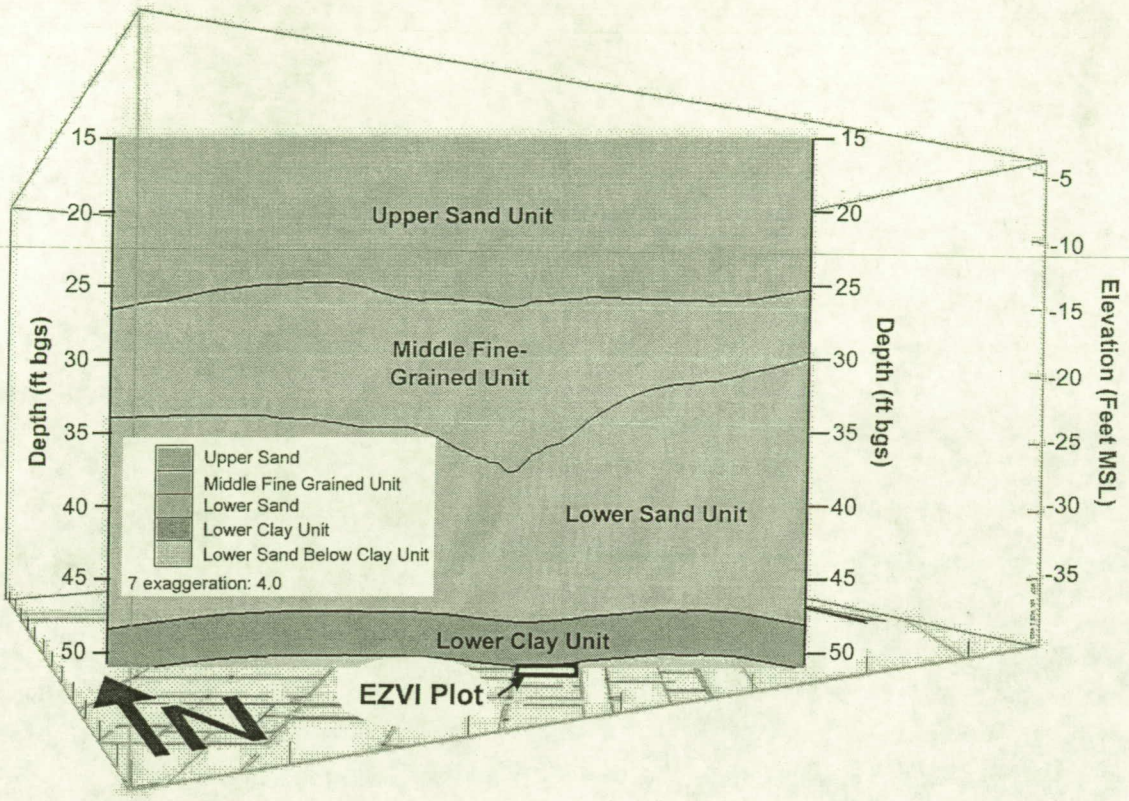


FIGURE 3. NW-SE Geologic Cross Section through the EZVI Plot.

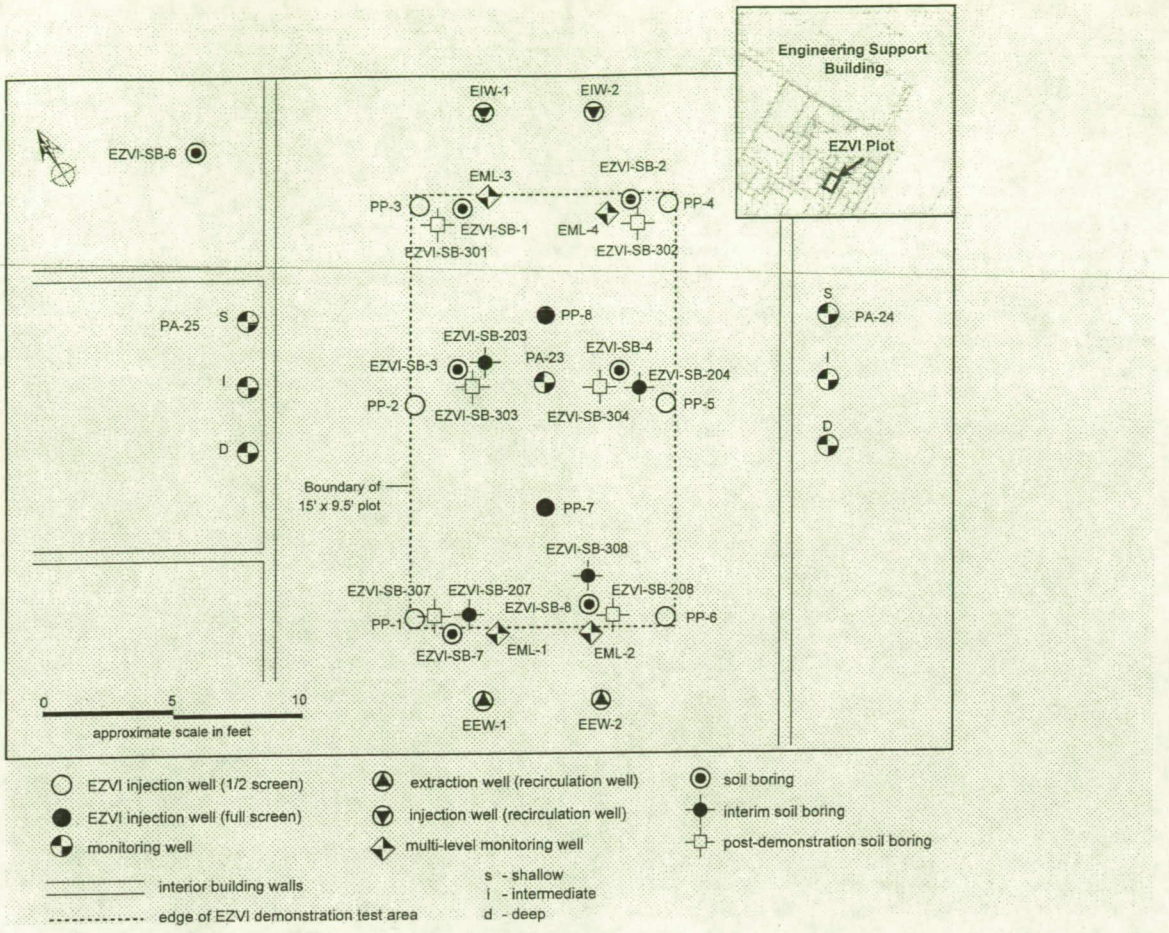


FIGURE 4. Sampling and monitoring locations within the demonstration test area.

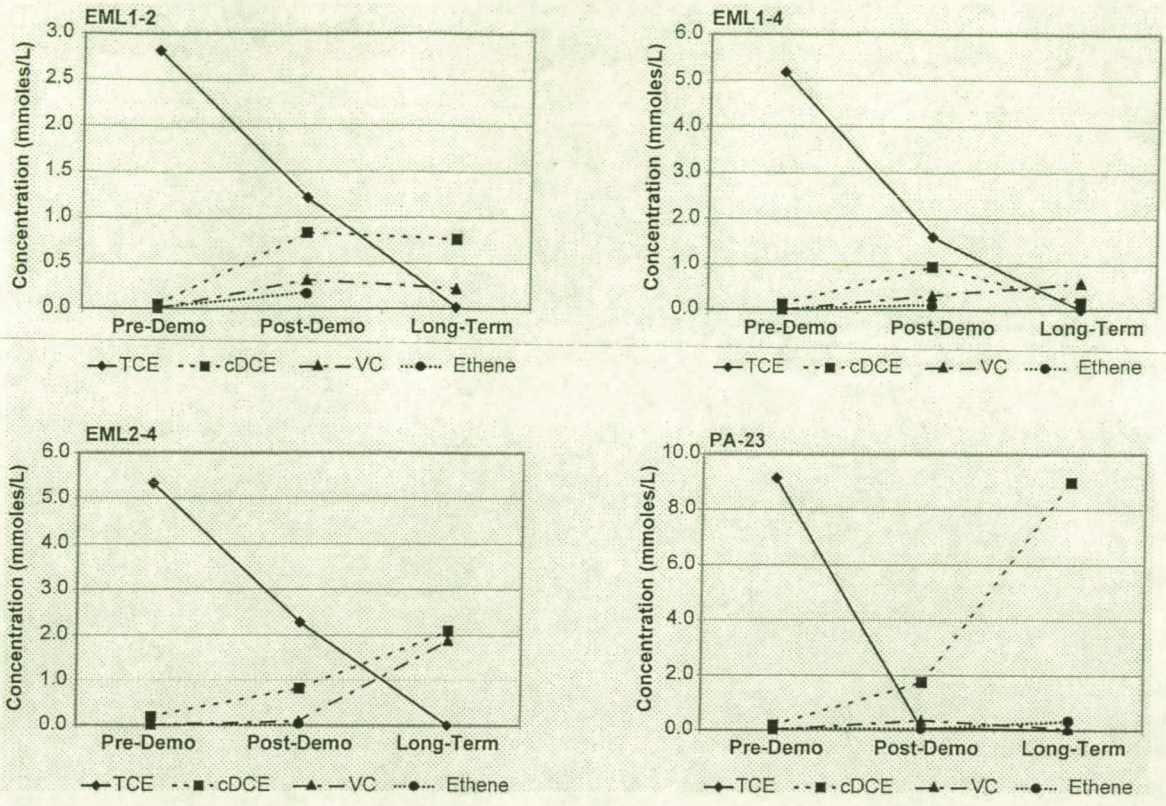


FIGURE 5. TCE, cDCE, VC and Ethene molar concentrations in selected monitoring wells over time.

TABLE 1. Volumes of EZVI Injections

Injection Location	Depth (ft bgs)	EZVI (gal)	Water (gal)
PP-1	16 - 20.5	40	96
	20.5 - 24	25	81
PP-2	16 - 20.5	154	170
	20.5 - 24	25	154
PP-3	16 - 20.5	15	51
	20.5 - 24	25	120
PP-4	16 - 20.5	25	27
	20.5 - 24	15	140
PP-5	16 - 20.5	15	50
	20.5 – 24	25	112
PP-6	16 - 20.5	40	88
	20.5 – 24	25	91
PP-7	16 - 20.5	102	172
	20.5 – 24	35	72
PP-8	16 - 20.5	60	110
	20.5 – 24	35	93

TABLE 2. Summary of TCE Concentrations Pre-, Interim, and Post-Demonstration Cores

Top Depth	Bottom Depth	Pre-Demo SB-1	Post-Demo SB-301	Pre-Demo SB-3	Inter-Demo SB-203	Post-Demo SB-303	Pre-Demo SB-4	Inter-Demo SB-204	Post-Demo SB-304
10	12	1	1	0	1	1	0	0	0
12	14	3	4	1	1	1	6	1	0
14	16	6	1	7	13	4	6	1	ND
16	18	87	1	**6,067**	1	1	45	1	ND
18	20	282	12	209	**1,023**	**451**	161	6	2
20	22	208	8	195	**798**	7	171	3	1
22	24	230	0	253	**495**	**4,502**	249	35	ND
24	26	283	NA	272	2	17	289	183	ND
26	28	263	119	252	NA	45	255	NA	28
Average for 16 to 24 feet		202	5	1681	579	1240	157	11	1
% Reduction		--	**97%**	--	**66%**	**26%**	--	**93%**	**99.5%**

Top Depth	Bottom Depth	Pre-Demo SB-2	Post-Demo SB-302	Pre-Demo SB-7	Inter-Demo SB-207	Post-Demo SB-307	Pre-Demo SB-8	Inter-Demo SB-208	Post-Demo SB-308
10	12	ND	1	0	1	2	2	ND	1
12	14	1	1	2	ND	1	2	ND	0
14	16	10	11	70	ND	0	21	ND	NA
16	18	89	5	**1,167**	ND	NA	127	ND	0
18	20	182	57	207	54	23	136	ND	NA
20	22	233	NA	175	ND	NA	157	NA	177
22	24	262	18	202	268	19	162	143	130
24	26	259	7	222	177	149	212	NA	125
26	28	270	8	268	NA	175	237	NA	NA
Average for 16 to 24 feet		192	27	438	81	21	146	48	102
% Reduction		--	**86%**	--	**82%**	**95%**	--	**67%**	**30%**

Concentrations of TCE presented in mg/Kg of dry soil

Bold values indicate suspected DNAPL based on threshold concentration of 300 mg/Kg

Bold border indicates target depth interval for injection of EZVI

Shading denotes visual evidence of EZVI at the sample depth.

NA - Not available - insufficient soil sample recovered from core ND - below detection limit

TABLE 3. Estimated Total TCE and TCE-DNAPL Mass Reduction by Linear Interpolation

Stratigraphic Unit	Pre-Demonstration Total TCE Mass (kg)	Pre-Demonstration TCE-DNAPL Mass (kg)	Post-Demonstration Total TCE Mass (kg)	Post-Demonstration TCE-DNAPL Mass (kg)	Change in Mass (%) Total TCE	Change in Mass (%) TCE-DNAPL
Upper Sand Unit (treatment interval)	17.8	3.8	2.6	0.6	86	84
Middle Fine-Grained Unit(a)	11.8	1.5	6.9	0.5	N/A	N/A
Lower Sand Unit(a)	0.12	0.0	0.10	0.0	N/A	N/A

(a) Any EZVI treatment of the Middle Fine-Grained Unit and Lower Sand Unit was incidental and these two units were not targeted during the injection.

N/A = not applicable.

TABLE 4. Estimated Total TCE Mass Reduction by Kriging

Stratigraphic Unit	Pre-Demonstration Total TCE Mass Average (kg)	Pre-Demonstration Total TCE Mass Lower Bound (kg)	Pre-Demonstration Total TCE Mass Upper Bound (kg)	Post-Demonstration Total TCE Mass Average (kg)	Post-Demonstration Total TCE Mass Lower Bound (kg)	Post-Demonstration Total TCE Mass Upper Bound (kg)	Change in Mass (%) Average (%)	Change in Mass (%) Lower Bound (%)	Change in Mass (%) Upper Bound (%)
Upper Sand Unit (treatment interval)	28	10	46	11.7	2.5	21	58	22	100
Middle Fine-Grained Unit(a)	6.6	6	8	5.9	5	7	N/A	N/A	N/A
Lower Sand Unit(a)	0.2	0.05	0.4	0.1	0.06	2	N/A	N/A	N/A
Total (Entire Plot)	35.2	16.5	54.5	17.8	8.5	27.1	N/A	N/A	N/A

(a) Any EZVI treatment of the Middle Fine-Grained Unit and Lower Sand Unit was incidental and these two units were not targeted during the injection.

N/A = not applicable.

TABLE 5: TCE concentrations in groundwater in multilevel wells and PA-23 before and after EZVI injection.

		TCE (mg/L)			cDCE (mg/L)			VC (mg/L)			Ethene (mg/L)		
Sample Location	Depth (ft bgs)	Pre-Demo	Post-Demo	Long-Term	Pre-Demo	Post-Demo	Long-Term	Pre-Demo	Post-Demo	Long-Term	Pre-Demo	Post-Demo	Long-Term
E-ML1-1	16	2.6	<0.02	na	0.54	0.03	na	<0.5	0.05	na	<0.5	0.13	na
E-ML1-2	18.5	370	160	2.4	4.8	81	74	<0.5	20	14	<0.5	4.8	na
E-ML1-3	21	450	92	2.7	11	76	78	<0.5	20	34	<0.5	6.7	na
E-ML1-4	23.5	680	210	<1.0	13	92	16	<0.5	20	37	<0.5	2.6	na
E-ML1-5	26	600	130	na	9.8	190	na	<0.5	29	na	<0.5	3.1	na
E-ML2-1	16	3.9	0.3	na	2.2	0.68	na	<0.2	20	na	<0.2	3.5	na
E-ML2-2	18.5	20	0.8	<0.2	1.1	44	8.8	<0.2	8.3	2.2	<0.2	4.2	na
E-ML2-3	21	350	76	1.0	21	86	5.3	<0.5	19	5.0	<0.5	4.7	na
E-ML2-4	23.5	700	300	<1.0	19	80	203	<0.5	5.9	118	<0.5	1.2	na
E-ML2-5	26	630	720	na	45	25	na	<0.5	<0.5	na	<0.5	<0.5	na
PA-23	16-26	1200	8.8	<0.02	17	170	870	<1.0	22	3.6	<0.5	1.7	9.3

Pre-Demo - July 2002 (March 2002 for PA-23)

Post-Demo - Nov 2002

Long-Term - Dec 2003 (March 2004 for PA-23)

na – sample not collected

Bold border indicates target depth interval for injection of EZVI

TABLE 6: TCE concentrations in perimeter monitoring wells.

	TCE (mg/L)			cDCE (mg/L)			VC (mg/L)		
Well ID	Pre-Demo	Demo	Post-Demo	Pre-Demo	Demo	Post-Demo	Pre-Demo	Demo	Post-Demo
PA-24S	772	474	12	47	16	32	<1	<50	1.58
PA-24I	258	110	86	149	161	181	0.14J	1.07	0.78
PA-24D	469	497	656	62	83	99	0.11J	0.59	0.16J
PA-25S	71	70	129	69	9	43	<1	<0.1	0.075J
PA-25I	534	784	944	116	104	91	<0.5	<0.1	0.17J
PA-25D	3	36	53	61	101	117	<0.05	0.14	0.35

Pre-Demo – March 2002
Demo – August 2002
Post Demo – November 2002
J – estimated value, below the laboratory reporting limit

One Sentence Summary for Table of Contents:

Results of the first field-scale demonstration of nano-scale emulsified zero-valent iron (EZVI) to enhance *in situ* dehalogenation of dense, non-aqueous phase liquids (DNAPLs).