A Pilot Scale EZVI and ZVI Treatment of Unsaturated and Saturated Soil for TCE Reduction

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ABSTRACT: Enhanced biological reductive dechlorination, micro-scale zero valent iron (ZVI), and emulsified zero valent iron (EZVI) injections were implemented to treat chlorinated volatile organic compounds (CVOCs) at a former manufacturing facility in western South Carolina. These remedial approaches – until recently typically implemented as standalone technologies – were combined to achieve synergistic reductions of tetrachloroethene (PCE), trichloroethene (TCE), and their reaction products. A total of 38 injections were made over the course of two days in both the unsaturated and saturated zones. The groundwater results from three shallow monitoring wells inside the injection area showed at least 50% reduction in dissolved concentration of PCE and TCE within a year of injection. There was a coincident increase in the appearance of daughter products such as cis-1,2-dichloroethene (cis-1,2-DCE), indicating that reductive dechlorination was occurring. Monitoring also shows reducing conditions persist in the injection area. Analytical results from unsaturated soil sampled after the injections showed all CVOC contaminants to be below USEPA industrial soil standards.

INTRODUCTION: PCE and TCE contamination – due to operational releases, apparently associated with a drum storage area – was discovered in soil and groundwater at a now closed manufacturing facility in western South Carolina.

Hydrogeologic Setting. The soil column is as follows: beneath paving and about 1 foot of fill, extending to a depth of approximately 9 to 11 feet (2.75-3.35 m) below ground surface (bgs) is red, silty clay with tan fine-grained mottling, and traces of mica; very faint relict of crystalline texture; soft, mealy; in places loose, and extremely friable. Below this layer, the lithology turns more saprolitic; dark brown with occasional coarse granular texture to 17 feet (5.2 m) bgs; soft and loose from 15 to 17 (4.6 – 5.2 m) feet bgs; brown, soft, silty clay texture, with coarse granular veining from 17 to 18 (5.2 – 5.5 m) feet bgs; brown with white thinly veined, gneissic pattern and mealy, friable, silty clay texture. The section becomes moist at approximately 8 feet (2.4 m) bgs and the saturated zone has been encountered between 11 and 14 feet (3.35 – 4.3 m) bgs. Top of bedrock is about 29 feet (8.8 m) bgs.

Shelby tube samples from the area exhibited high porosities but low vertical permeability (less than 0.2 feet (6 cm) per day), characteristic of finer grained material. Groundwater is present in the saprolite under unconfined conditions. The saprolite acts as one unit, i.e., no upward or downward gradients. Rising and falling head slug tests indicated a hydraulic conductivity on the order of 8E-04 centimeters per second (cm/sec), and piezometry indicates a gradient in the area of about 0.02 ft/ft, yielding an effective lateral velocity of about 2 feet per day.

Source Action Pilot Design. In March 2007, a pilot scale injection program was implemented to treat sorbed and dissolved CVOC mass in the immediate area. The area chosen for the program had been characterized and identified through sampling as an ongoing source of site groundwater contamination.

The pilot was designed with the intent of manipulating both geochemical and biological conditions in the subsurface. We sought to reduce source area residual CVOC mass by combining three established technologies: direct injection of micro-scale ZVI (with oxygen scavengers), micro-scale ZVI suspended in oil emulsion, and carbon substrate along with vitamins and nutrients. In this manner, we expected to: address sorbed CVOC mass and the soil gas in the entire soil column, and enhance the naturally occurring biotic and abiotic reductive dechlorination of aqueous CVOC.

The first set of injections consisted of emulsified zero-valent iron applied only to the unsaturated soil in a subset of the source area. The client had requested that unsaturated soil be addressed in-situ – if possible avoiding the installation of mechanical equipment and attendant operations and maintenance. Extraction would have been difficult due to the culture in the area and soil type, and injection galleries to support enhanced biological degradation would not have been effective without some O&M attention.

EZVI has historically been used to enhance the destruction of chlorinated DNAPL in source zones by creating intimate contact between dense non-aqueous phase liquids (DNAPL) and the ZVI particles. The EZVI is composed of a biodegradable, food-grade surfactant, vegetable oil, water, and ZVI particles (micro-scale iron), which form emulsion particles that contain the ZVI particles in water surrounded by an oil-liquid membrane. Due to their small size, these EZVI/oil particles may remain in suspension in groundwater and move down-gradient of an injection point with the flow of groundwater.

Since the exterior oil membrane of the emulsion particles has hydrophobic properties similar to that of DNAPL, the emulsion is miscible with the DNAPL. It is believed that as the oil emulsion droplets combine, for example, with pure-phase TCE, the TCE dissolves and diffuses into the aqueous droplet containing ZVI that resides within the oil emulsion droplet. It is also believed that the final degradation by-products from the dechlorination reaction are driven by the increase in concentration inside the aqueous emulsion droplet to diffusion out into the non-aqueous phase (oil and TCE), and from there out into the surrounding aqueous phase (Brooks, 2000). While the ZVI particles in the aqueous emulsion droplet remain reactive, the chlorinated compounds are continually degraded within the aqueous emulsion droplets, thus maintaining a concentration gradient across the oil membrane and establishing a driving force for additional TCE migration into the aqueous emulsion droplet, where additional degradation can occur.

A second, deeper (saturated zone) injection covered a wider area, and consisted of sodium sulfite (as an oxygen scavenger), nutrients, calcium propionate solution, zero-valent iron (ZVI) suspension, yeast extract, and liquid hydrogen release compound (HRC®-X and HRC®) to achieve the following:

- promote anaerobic conditions in groundwater with both the ZVI and substrate

- rapidly decrease higher concentrations on contact with ZVI
- support indigenous bacteria in the subsurface with ample nutrients
- slowly release hydrogen, also to support reductive biodegradation

MATERIALS AND METHODS: The pilot scale injection program included a total of 38 injections, twenty-two in the saturated zone and sixteen in the unsaturated zone. Injections were performed at 10-12 feet (3-3.65 m) below ground surface (bgs) and 14-16 feet (4.25-4.9 m) bgs in the saturated zone and at 6.5-8 feet (2-2.4 m) bgs and 8.5-10 feet (2.6-3 m) bgs in the unsaturated zone. Injection depths were prescribed to target more permeable layers as identified during site characterization, hypothesized to be preferential pathways for dissolved-phase CVOC flux.

IET uses proprietary tooling and an injection process that first introduces compressed gas at moderate pressure (100 to 175 psi or 7 to 12.3 kg/cm) to the subsurface, followed immediately by the remedial slurry without releasing the back pressure in the probe. With this process approach, pore water is displaced both laterally and vertically. The overall effect is an in-situ mixing and homogenization of the subsurface conditions.

RESULTS AND DISCUSSION: Prior to the injection, monitoring wells were installed to monitor remedial performance in the saturated treatment area. Three of the monitoring wells, TWM-19, TWM-28, and TWM-29, experienced a significant reduction in CVOC concentrations within a year or less. The location of the monitoring wells and soil borings are shown in Figure 1. The location of the saturated and unsaturated treatment areas are seen in Figure 2. TWM-27, not discussed, is furthest from source and on the fringes of injection area, but concentrations have tapered off from a lower baseline here as well.

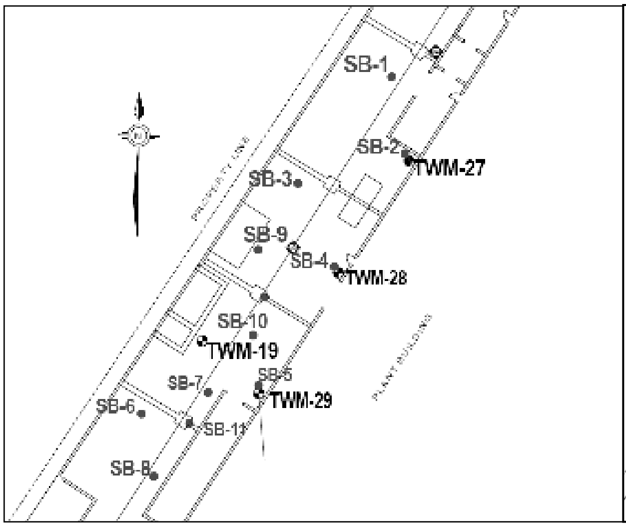

FIGURE 1: Map of Monitoring Well and Soil Boring Locations

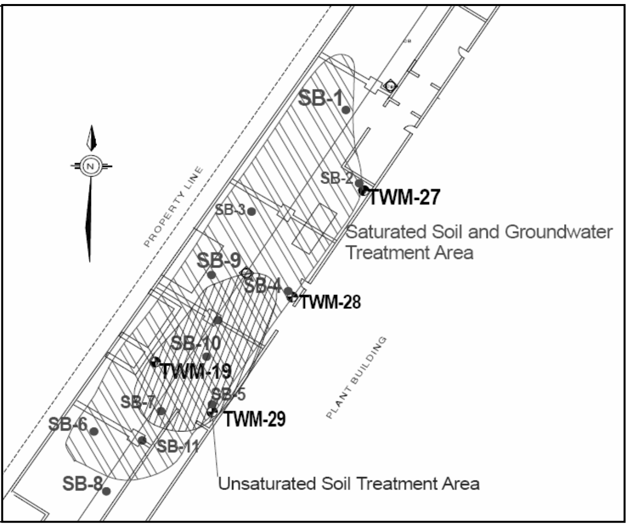

FIGURE 2: Map of Saturated and Unsaturated Treatment Areas

TWM-19: This well is located at the perimeter of the unsaturated soil injection area and well within the saturated zone treatment area. The concentrations of PCE and TCE in monitoring well TW-19 have decreased significantly since the March 2007 injection event. The concentration of PCE decreased 51.1% (from 176 µg/L to 86 µg/L), and that of TCE decreased 57.9% (from 180 µg/L to 75.7 µg/L). As would be expected, the concentration of cis-1,2-DCE increased from 155 µg/L to 583 µg/L. These trends are seen in Figure 3. There is also an associated increase in dissolved gases and chlorides, which indicates that complete reductive dechlorination is occurring in this area.

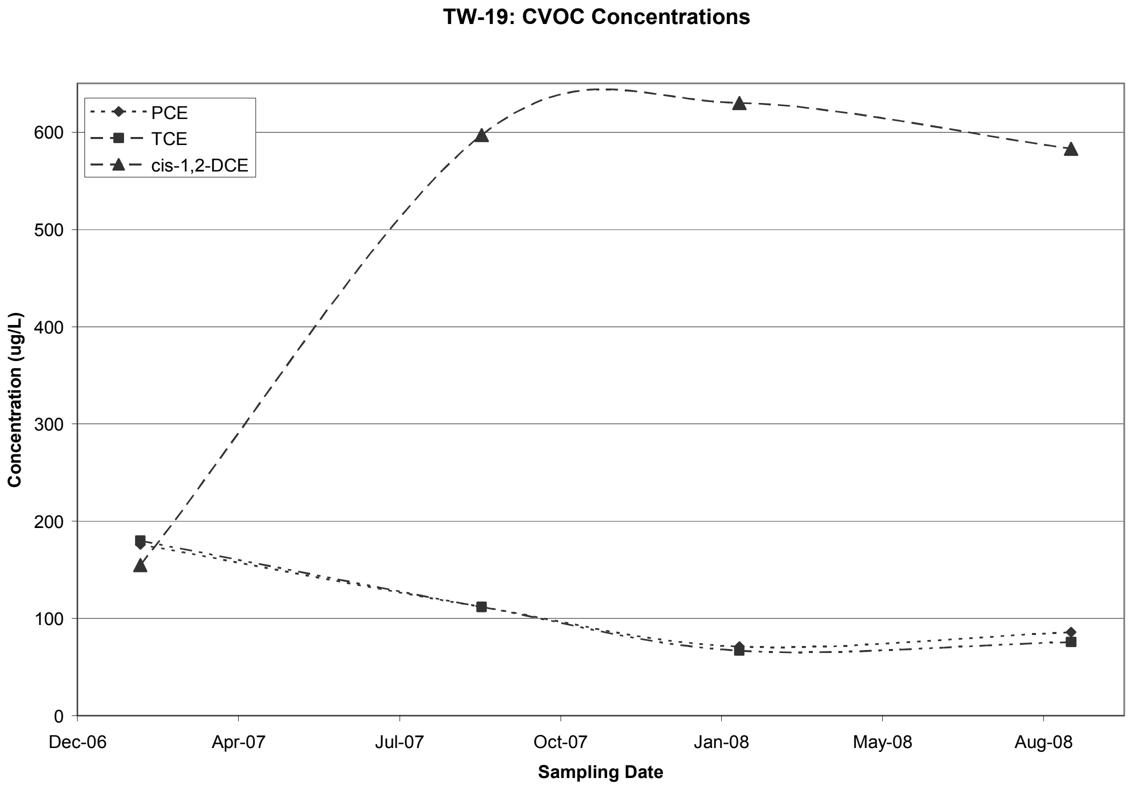

FIGURE 3: CVOC Concentration for TWM-19

TWM-28: This well is located at the perimeter of both the unsaturated and saturated zone injections area, and yet appears not to have been directly influenced by either injection. This may be a result of a non-radial distribution of the injectants. The distribution pattern and its axis are most likely influenced by the structure less than 5 feet southwest of the well. The footings and the compacted soil beneath the building, in conjunction with the previous injections northwest, contributed to the north and northwest distribution of the injected materials. No injection occurred between the well and the structure.

As in TWM-27, an increase in dissolved iron is a product of the up-gradient injections. The lack of an associated cis-1,2-DCE increase with the TCE decrease in conjunction with the transient increase in mother products following the injection also points to the well's data being more the result of an up-gradient source than mass sorbed to soil in the area. This data is seen in Table 1.

TABLE 1: TW-28 CVOC Concentrations

Sampling Date	*Feb-07*	*Sep-07*	*Feb-08*	*Sep-08*
PCE	441	522	346	298
TCE	1,820	2,270	1,560	1,400
cis-1,2-DCE	101	166	133	94.9

TWM-29: This well is centrally located in both of the injection grids, and appears to have been the most strongly influenced by the injection event. PCE concentrations in TW-29 have decreased by 93.6% with concentrations decreasing from 175 µg/L to 11.2 µg/L. TCE concentrations have decreased by 66.5% from 361 µg/L to 121 µg/L. cis-1,2-DCE concentrations initially increased, but have since decreased 39% from 62.8 µg/L during the baseline sampling event to 38.3 µg/L during the September 2008 sampling event. These concentration trends are seen in Figure 4.

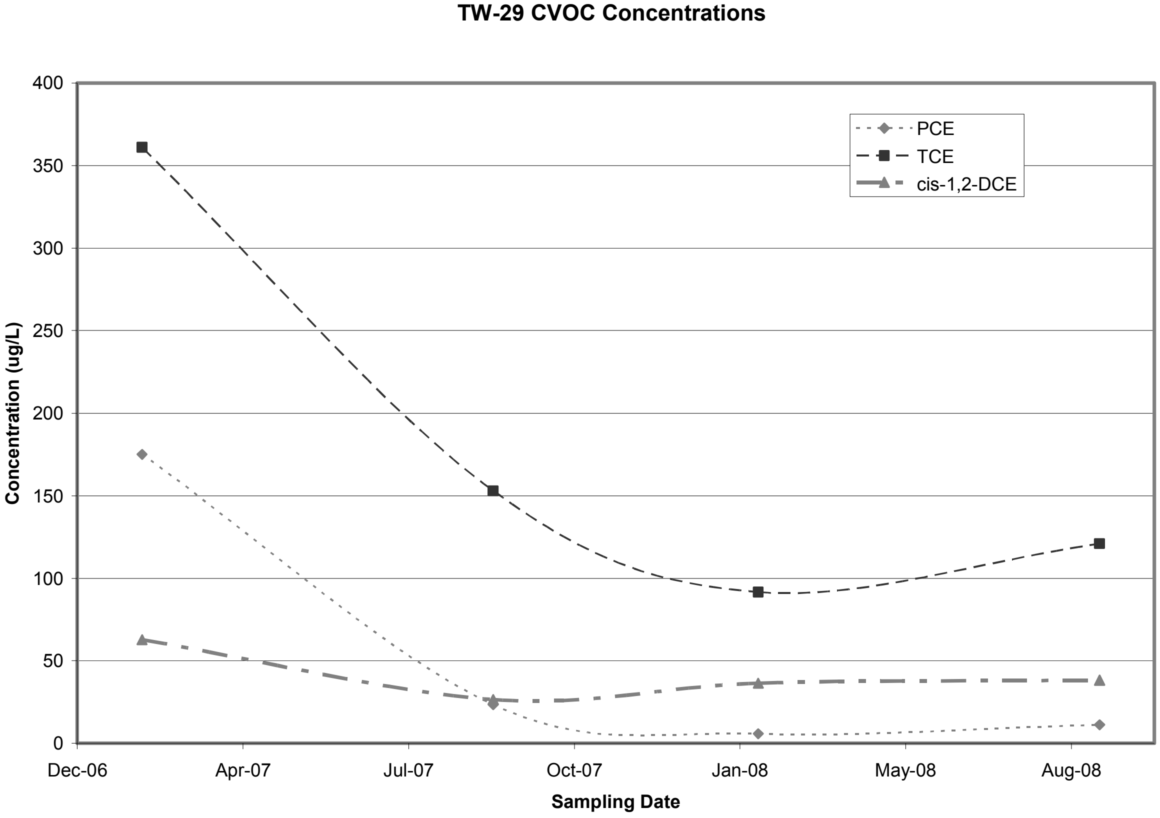

FIGURE 4: CVOC Concentrations for TWM-29

Unsaturated Soil Injection Results. Soil samples were also collected from the unsaturated zone (6 ft to 8 ft or 1.8 to 2.4 m bgs) to confirm the effectiveness of the EZVI application. While recognizing the difficulty in drawing inferences from with limited baseline and follow-up soil grab sampling, the weight of evidence points to a positive response. The concentrations of PCE and TCE in the area of the EZVI injections generally decreased, and in a few cases, cis-1,2-DCE concentrations increased.

SB-4. SB-4 is somewhat removed from the assumed point of release. The baseline contamination was seen only at depth. Pilot injection appears to have had some effect, without the appearance of daughter products in the unsaturated soil. Target compounds TCE and PCE were effectively removed as seen in Figure 5 below:

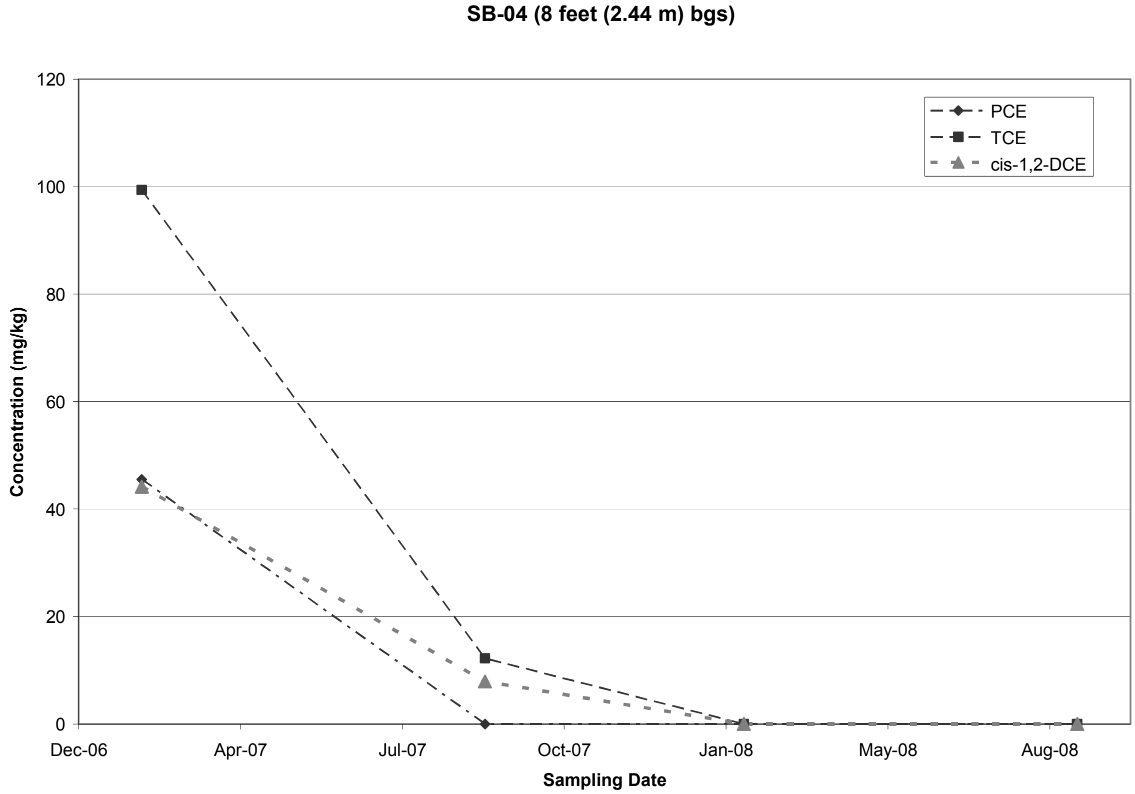

FIGURE 5: Soil CVOC Concentrations at SB-4

SB-06: Not all samples exhibited such obvious and repeatable reduction. Target compound concentrations in soil samples at SB-06 at first post-injection sampling decreased two orders of magnitude. However in two follow-up sampling events, PCE and TCE concentrations reverted back to the same magnitude as baseline. In the same samples, cis-1,2-DCE concentrations increased substantially, from 103 µg/kg (baseline) to 2,340 µg/kg.

SB-07: PCE and TCE concentrations have decreased, nominally by an order of magnitude to the mg/kg level in SB-7, which is located at the edge of the injection area. Concentrations of cis-1,2-DCE have decreased in SB-07 from 167 µg/kg during the baseline sampling event to 104 µg/kg during the September 2008 sampling event. Here too, subsequent follow-up samples showed cis-1,2-DCE jump to the 100 to 1000 mg/kg range. The sample results are in posted for all three CVOC in Figure 6.

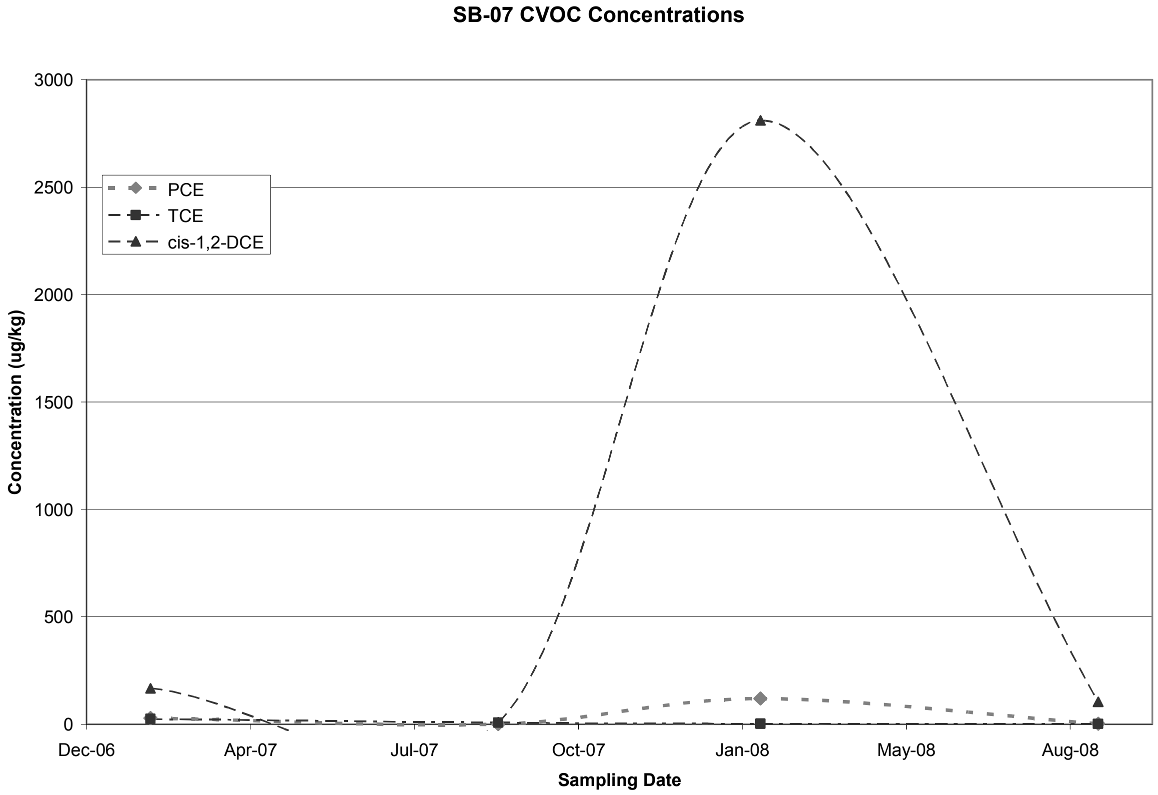

FIGURE 6: Soil CVOC Concentrations in SB-07

SB-10 and SB-11: Results from these soil boring stations, in the center of the EZVI injection area, have exhibited similar trends as SB-7. In SB-10 samples, parent compound (PCE and TCE) concentrations have dropped nearly two orders of magnitude to the mg/kg range, while cis-1,2-DCE dropped from nominally 100 mg/kg to about 10 mg/kg. The concentrations of all the CVOCs dropped smoothly, but less significantly in SB-11, by a factor of about 10.

CONCLUSIONS: As of Fall 2008, the concentrations of CVOCs in the source zone groundwater wells have generally decreased about 20% since the injection March 2007 injection event, with the parent compound (PCE and TCE) concentrations about halving in the three nearest performance monitoring wells. In the two most clearly affected and closest to release area monitoring wells, TWM-19 and TWM-29, the concentrations of parent compounds decreased more significantly, with reduction ranging from 50% to over 90%. In the well nearest to the release (TWM-19), cis-1,2-DCE concentrations jumped significantly and have since held steady or decayed somewhat. A February 2009 re-sampling groundwater indicates those trends continue apace in every well. Concentrations of CVOCs in soil have also decreased significantly since the injection of EZVI. Soil boring sample CVOC concentrations within the treatment area have generally dropped 90%.