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## Longevity of EHC<sup>®</sup> Treatment

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EHC<sup>®</sup> is an integrated combination of controlled-release plant-derived carbon plus micro-scale zero valent iron (ZVI) particles used for stimulating in situ chemical reduction of otherwise persistent organic compounds in groundwater. EHC-M<sup>®</sup> uses the same combination plus a source of sulphate (if needed) to promote the precipitation of dissolved metals. In evaluating the longevity of EHC, several consumption mechanisms of the reactive components need to be considered:

- ZVI oxidation and carbon fermentation due to consumption (reduction) of terminal electron acceptors (TEAs), such as dissolved oxygen (DO), nitrate and sulfate;
- Anaerobic corrosion of ZVI;
- Organic contaminant reduction; and
- Trace metal reduction and precipitation.

These processes are not independent of one another and are also controlled by site conditions such as groundwater flow velocity, inorganic aqueous concentrations, VOC concentrations and temperature. Although it is somewhat difficult to separate the longevity of the iron from that of the carbon given that they are present together, theoretical calculations supported by results from long-term laboratory studies and mature field sites can be used to estimate the effective lifetime of EHC.

### 1.1 Theoretical Considerations - Iron Consumption

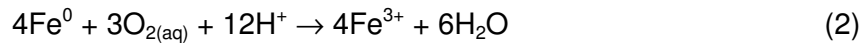
To evaluate potential rates of ZVI consumption in EHC, the following theoretical calculations due to reactions with VOCs and inorganic electron acceptors are presented for a hypothetical site, but similar calculations can be performed using site-specific data. The hypothetical site used in the calculations contains 2 mg/L DO, 5 mg/L of trichloroethene (TCE), 5 mg/L nitrate and 20 mg/L sulphate. The groundwater flow velocity at the site is assumed to be 0.10 m/day and aquifer porosity 0.25. An assumed EHC-amended zone is 6 m wide was amended with 0.5% EHC (0.2%ZVI) per soil mass. The ZVI consumption calculations are based on a unit cell with a face surface area of 1 m<sup>2</sup> of the EHC-amended zone or a volume of 6 m<sup>3</sup> of EHC-amended aquifer, containing about 22 kg of ZVI. A worse case scenario was assumed; that is the carbon electron donor in EHC was not included in the electron acceptor consumption calculations.

Water corrosion (oxidation) of granular iron is an important ZVI consumption process, resulting in ferrous iron, hydrogen gas and hydroxide ion production and an increase in pH and decline in Eh:



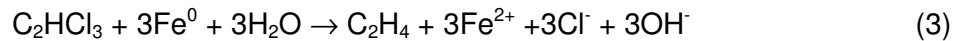
Tests conducted with different types of ZVI materials have indicated in water corrosion rates on the order of 0.1 to 0.6 mmol/kg Fe/day, with a value of 0.3 mmol/kg Fe/day measured for particulate ZVI used in EHC (Reardon, 2005). The iron-water corrosion rate is independent of groundwater flow velocity. Based on the water corrosion rate of 0.3 mmol/kg Fe/day, the annual iron consumption due to water corrosion at this hypothetical EHC site would be 135 g/yr. This is equivalent to about 0.6% of the total ZVI present in the 6 m wide EHC-amended zone.

Any dissolved oxygen will also corrode (consume) the ZVI:



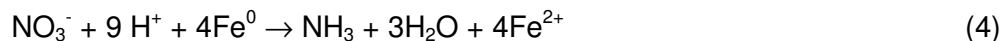
Based on the above assumptions, the annual amount of DO (2 mg/L or 0.063 mmol/L) entering the unit cell of EHC-amended zone would be 18 g/yr (0.57 mole/yr). Since, four moles of iron are consumed for every three moles of DO, the annual iron consumption rate would be 43 g/yr (0.76 mol/yr). This iron amount represents about 0.2% of the total ZVI in the EHC-amended zone.

Complete reductive dechlorination of TCE and the corresponding ZVI oxidation can be expressed by the following:



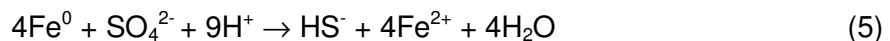
Thus, the annual amount of TCE (5 mg/L or 0.038 mmol/L) entering the unit cell of EHC-amended zone would be 46 g/yr (0.35 mole/yr). Since three moles of iron are consumed for every mole of TCE, the annual iron consumption rate would be 58 g/yr (1.04 mol/yr) or 0.3% of the available ZVI mass in the EHC-amended zone.

If present, nitrate reduction by granular iron results in the production of ammonia/ammonium:



Complete reduction of 5 mg/L of nitrate (0.08 mmol/L) by ZVI would result in consumption of an annual nitrate mass flux into the unit cell of EHC-amended zone of 46 g/yr (0.74 mol/yr). Four moles of iron are consumed for every mole of nitrate; therefore the annual consumption rate would be equal to 165 g/yr (2.94 mol/yr) or 0.8% of the ZVI available.

Sulphate ( $\text{SO}_4^{2-}$ ) in the presence of iron may undergo reduction to sulphide:



If complete sulphate reduction occurred due via ZVI oxidation, the annual amount of sulphate (20 mg/L or 0.21 mmol/L) entering the unit cell of EHC-amended zone would be 183 g/yr (1.9 mole/yr). Since four moles of iron are consumed for every mole of sulfate, the annual iron consumption rate would be 426 g/yr (7.6 mol/yr) or 2.0% of the ZVI available.

If electron acceptor reduction and VOC degradation do not compete with water corrosion of ZVI, the annual ZVI consumption rate would be about 4% of the ZVI available. This would result in a conservative ZVI lifetime in an EHC-amended zone of about 25 years at this hypothetical site.

In summary, many variables in groundwater chemistry can impact the consumption rate of ZVI in an EHC-amended zone. However, in most conditions, the ZVI particles should last for decades.

## **1.2 Theoretical Considerations - Carbon Consumption in VOC plumes**

As mentioned previously, the carbon component of EHC is comprised of fine-grained plant derived fibrous organic carbon particles. Because of the predominance of cellulose and hemicellulose in the particles, these particles will degrade more slowly (last longer) than other more soluble forms of carbon such as lactates, oils, and other glucose based amendments.

Carbon consumption (decay) in the subsurface is often assumed to follow a first order model. Under aerobic soil conditions, cellulose has been shown to persist over several months (Cheshire 1979, Kassim et al, 1981) and will degrade more slowly under anaerobic saturated conditions. In other studies, a first order carbon decay constant (K) of  $1.6E-3 \text{ day}^{-1}$  was obtained in cellulose columns used to promote denitrification exposed to a nitrate flux of about 70 to 75 mg/L nitrate-N at room temperature (Vogan 1993). This equates to a 50% loss of cellulose in about 300 days or 10 months. Lower rates of degradation (K of  $5E-4 \text{ day}^{-1}$ ) were obtained in sawdust columns exposed to the same flux. Sawdust contains a relatively higher proportion of hemi-cellulose and lignin. In-situ sawdust based denitrifying systems have operated for 15 years at field temperatures (Robertson et al, 2008).

Given that the carbon demand in the above conditions is far greater than that usually occurring in organic contaminant plumes (e.g. see 1.1), these published carbon degradation rates indicate that the carbon component of EHC should also last for years in the subsurface.

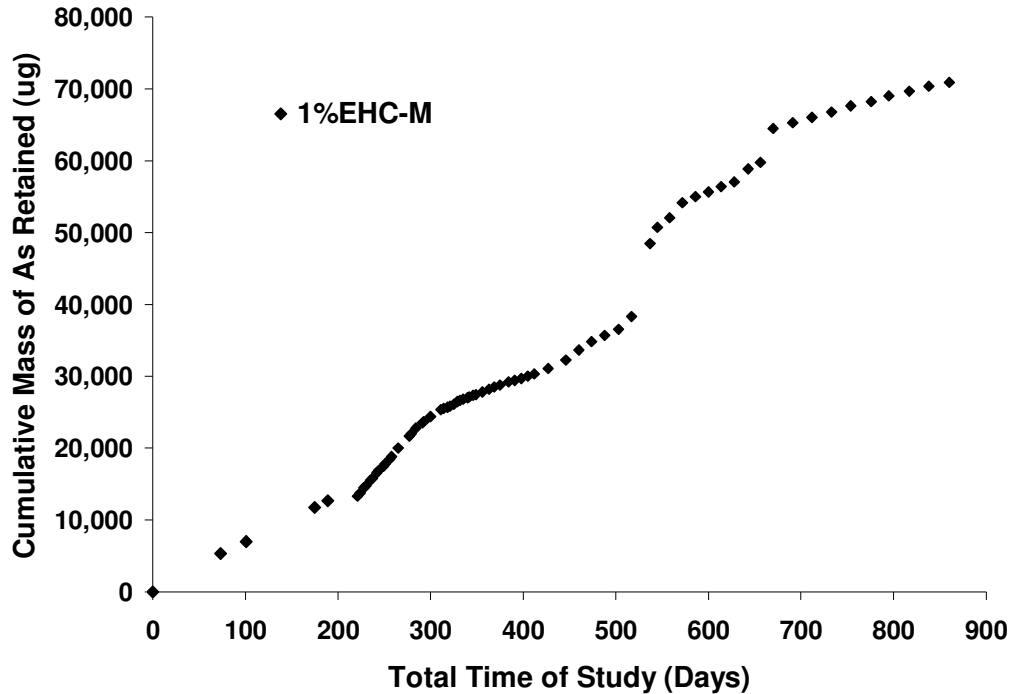
## **1.3 Theoretical Considerations- Trace Metal (arsenic) Removal**

The consumption of reactive material (iron, sorbent, carbon, or iron-carbon combinations) due to precipitation of metals is usually expressed in terms of removal capacity, in that these types of treatment zones will have a finite lifetime. The following calculations are presented for arsenic (As) treatment and EHC-M.

The primary mechanism of As removal in the presence of EHC-M (ZVI, organic carbon and sulfate) entails physical precipitation of arsenic with iron corrosion products, especially those associated with the reduction of sulfate to form arsenopyrite (Blowes et al., 2000, Kober et al., 2005; Craw et al., 2003). As noted above, it is anticipated that an EHC-M system will have a finite capacity for As treatment, based on the As flux and the amount of EHC-M applied, as the carbon and iron are consumed. From a long-term column test results with an

EHC-M/aquifer material mixture (Figure 1), a normalized As removal capacity of at least  $14 \text{ mg}_{\text{As}}/\text{g}_{\text{EHC-M}}$  is expected in an EHC-M amended aquifer zone.

Results of a sequential dissolution analysis performed on the column material after completion of the test indicated about 50% of the initial iron contained in EHC-M remained un-oxidized after 3 years of flow (Przepiora et al., 2008). Consequently, a sufficient amount of ZVI remained within the EHC-M column for an additional 2-3 years of ferrous iron generation.



**Figure 1. Cumulative mass of As retained within the EHC-M column in a long-term column experiment (6 inch long 1%<sub>wt</sub>EHC-M column, 2 inch diameter).**

An EHC-M longevity calculation was done for a representative cell of a proposed 0.3%<sub>wt</sub>EHC-M PRB (1 ft<sup>2</sup> face area, 20 ft long in the direction of flow, 25% porosity). In this case, we assumed a groundwater velocity at a site of 2 ft/day and an average As concentration of 2 mg/L. This equates to an anticipated mass flux of As in the cell of  $28 \text{ mg}_{\text{As}}/\text{day}$  ( $v \times A \times n \times C_{\text{As}} = 2 \text{ ft}/\text{day} \times 1 \text{ ft}^2 \times 0.25 \times 2 \text{ mg}/\text{L} \times 28.3 \text{ L}/\text{ft}^3$ ).

Using the As removal capacity above, about  $2 \text{ g}_{\text{EHC-M}}/\text{day}$  EHC-M would be used up every day in the cell ( $\text{Mass Flux}_{\text{As}} \div \text{As Removal capacity} = 28 \text{ mg}_{\text{As}}/\text{day} \div 14 \text{ mg}_{\text{As}}/\text{g}_{\text{EHC-M}}$ ). The amount of EHC-M held in the 20 ft<sup>3</sup> cell of 0.3%<sub>wt</sub>EHC-M is about 2,900 g (assuming an aquifer bulk density of 1.7 g/cm<sup>3</sup>). Therefore, the theoretical longevity of the proposed EHC-M zone is about 1,450 days (4 years) ( $2,900 \text{ g}_{\text{EHC-M}} \div 2 \text{ g}_{\text{EHC-M}}/\text{day}$ ).

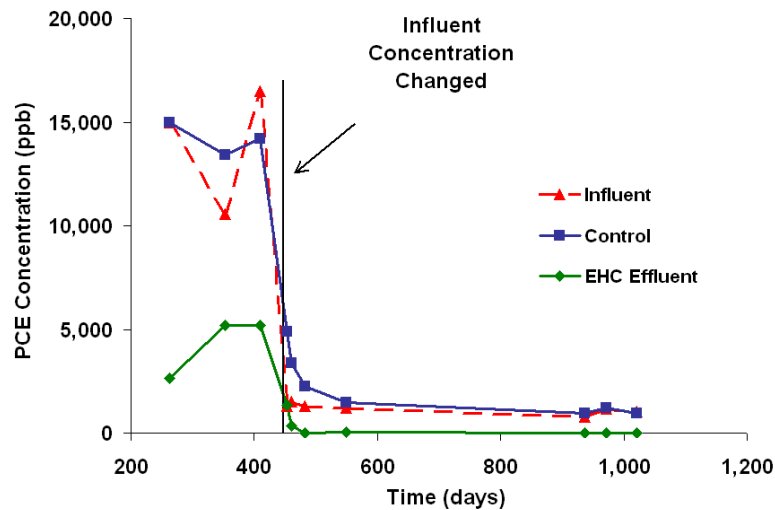
From the above theoretical considerations, it would appear that EHC (or EHC-M) has the potential to promote trace metal removal for an extended period at many field sites.

## 2.0 Observations of Carbon/ZVI Longevity in Column Studies

### 2.1 Column Study of PCE Degradation

The longevity of EHC was evaluated in a long-term (3 year) continuous-flow, laboratory column study to monitor the treatment of tetrachloroethylene (PCE) in groundwater (Dmitrovic, 2009, in preparation). A column was packed with a mixture of 5% EHC by weight and sand. During the first phase of the study the influent PCE concentration was set at 16,000 ppb and the flow rate maintained to create a contact time of approximately 0.3 days. The second phase of the study was initiated on day 450 to evaluate the performance of EHC at a PCE concentration and groundwater flow rate more representative of typical field conditions. During the second phase of the testing the feed concentration was decreased to about 1,900 ppb and the flow rate was reduced to create a contact time of approximately 1 day. In all cases, the columns were operated at room temperature.

Volatile organic compound (VOC) concentrations were monitored in the influent and effluents over time. During the initial phase of the study where the influent PCE concentration was maintained at 16,000 ppb, the EHC column supported between 50 and 80% removal of total VOCs (Figure 2). At the lower flow rate (day 461) a reduction in influent PCE from 1,500 ppb to 355 ppb in the EHC column was observed. The PCE concentrations in the EHC column effluent were further reduced (<50 ppb) in four subsequent sampling events, to non-detect (<20 ppb) on day 972. Trace concentrations of trichloroethylene (TCE) (<120 ppb) and cis-1,2-dichloroethene (cis-1,2-DCE) (<10 ppb) were detected during phase two. The control system showed no appreciable change in the PCE concentration.



**Figure 2. Influence of EHC on groundwater PCE concentrations.**

The physical sorptive capacity of the organic portion of EHC was estimated to be approximately 48 mg of PCE. Based on the initial PCE concentration of 16 mg/L and a flow

rate of 500 mL/day, the adsorptive capacity of the column would have been exhausted after 6 days. Thus, the decrease in PCE concentrations after day 6 can be attributed to either chemical or biological transformations and not temporary physical sequestration.

The EHC in this column was effective for approximately 2.8 years at room temperature. Assuming the carbon portion continues to be a significant contributor to the treatment, the longevity of the carbon should be greater at lower groundwater temperatures because the rate of microbial carbon consumption is expected to be lower. Applying a 'rule of thumb' that microbial activity would decrease by 50% for a 10° C decrease in temperature, one can hypothesize that the EHC may remain effective for over 5 years at lower groundwater temperatures.

## 2.2 Estimate of EHC Longevity from Perchlorate Column Study

A 99% removal efficiency continued to be achieved after 1200 days of continuous-flow operation of a column containing 24% by mass of EHC and sand exposed to influent perchlorate concentration of approximately 100,000 ppb (Figure 3). The high proportion of EHC was designed to simulate a PRB trench type application. The flow rate through the columns was maintained at 150 mL/day.

Following a short acclimation period, the EHC column reduced the perchlorate concentration from 120,000 ppb in the influent to 9,400 ppb, corresponding to a 92% removal (Figure 3). The perchlorate concentration was further reduced in a downstream soil microcosm to non-detect (detection limit = 200 ppb). This suggests that the removal mechanism for perchlorate is biologically controlled. The control system showed a slight (17%) decrease in the perchlorate concentration.

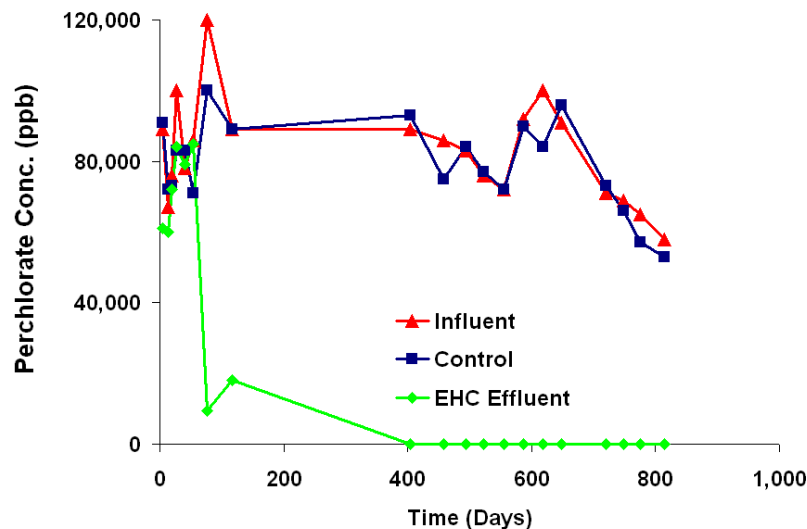


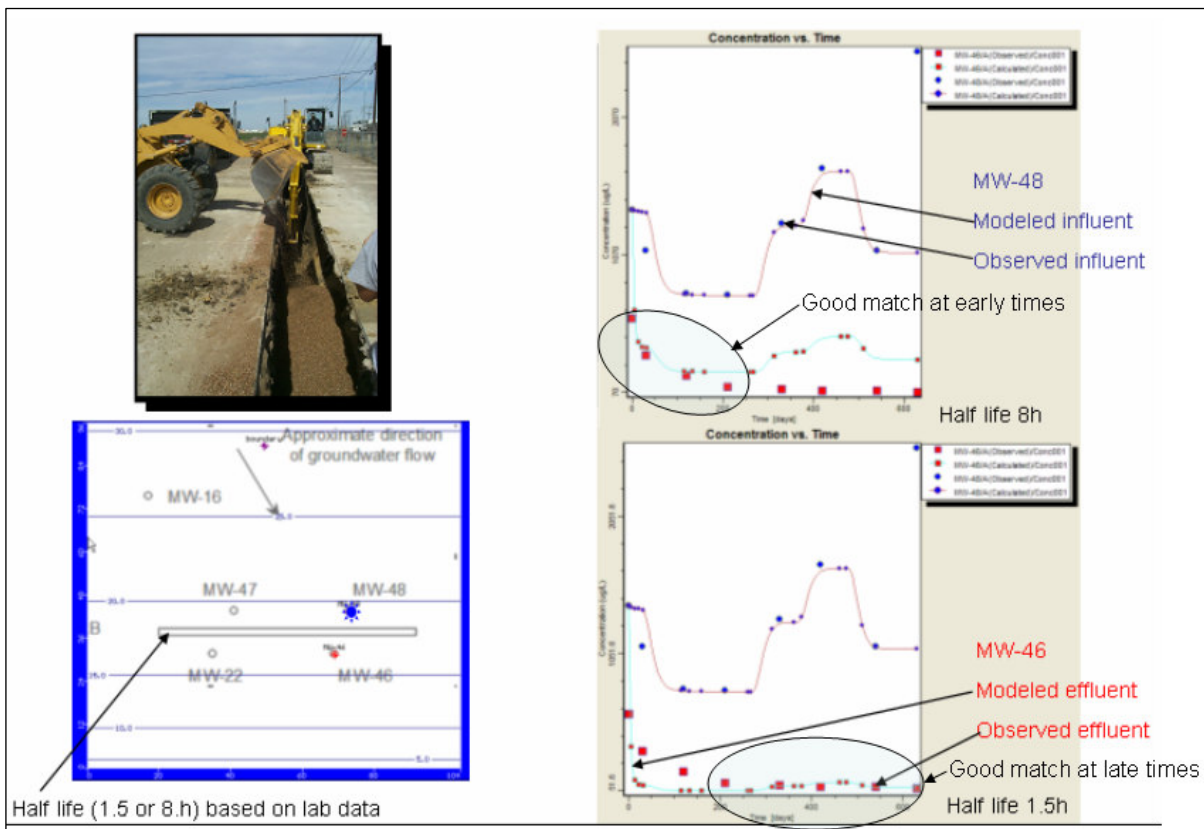
Figure 3. Influence of EHC on groundwater perchlorate concentrations.

Data from day 815 of the study showed that the EHC column continued to support complete reduction of perchlorate (detection limit = 2 ppb) while the control column showed little, if any, reductions. Subsequent to day 815, EHC removal rates remained stable but control column effluent decreased to about 50 % of the influent concentration, making interpretation of these data more difficult. Nevertheless, over three years of consistent removal of perchlorate in this EHC column (at room temperature) provides further encouraging evidence with respect to field –scale EHC longevity.

### 3.0 Estimate of EHC Longevity from Field Projects

#### 3.1 Trenched EHC PRB for Chloroethenes

A dissolved chloroethene plume migrating from a source zone through a thin permeable soil unit overlying bedrock was targeted for treatment at a site in the southern US.



**Figure 4. Trench PRB and Modeled Data**

A permeable reactive barrier (PRB) was constructed to intercept the dissolved groundwater plume (Figure 4). The PRB was constructed with an excavator by digging a 3-foot wide trench down to the top of the bedrock, followed by filling the bottom foot with a mixture of 10% EHC and sand. Only the bottom foot required filling because the groundwater table was

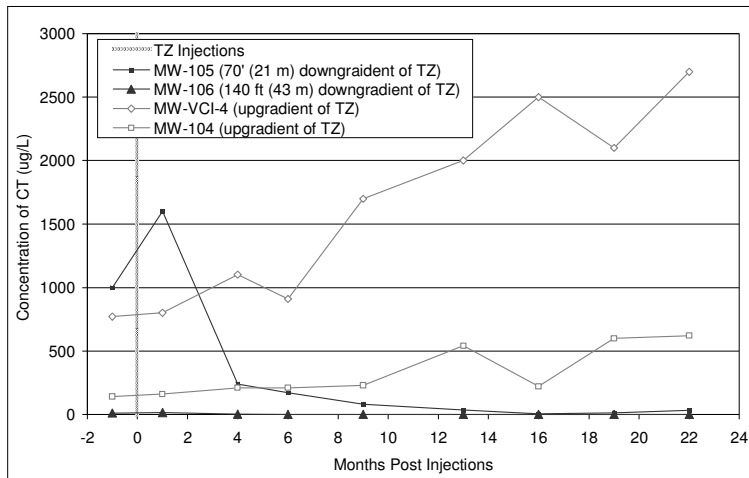
less than a foot above the bedrock, and the permeable soil unit was also at this depth. The remainder of the PRB was backfilled with pea gravel.

Two pairs of upgradient and downgradient monitoring wells were used to evaluate the effectiveness of the PRB and showed large reductions of all of the constituents present for 21 months of field observations.

The site was analyzed with a numerical model (Moreno et al, 2008). Bench scale data for PCE and breakdown products were available from a laboratory column study conducted in support of this application. Using these data, a model was prepared to analyze the expected concentrations downgradient of the trench. A single layer MODFLOW/RT3D model with uniform hydraulic gradient was applied. The trench was modeled as a zone of higher hydraulic conductivity and reactivity. Degradation inside the trench was modeled as first-order decay. The modeled data were compared to observed concentrations in the field (Figure 4). Six daughter products were also calibrated for a range of specified yield rates. The modeled results show that the effective half life of PCE inside the trench ranged from 8 hours at early times (first 200 days of operation) dropping to 1.5 hours thereafter, likely reflecting degradation rates due to integrated biological and abiotic reductive processes.

### 3.2 Carbon Tetrachloride Treatment using an Injected EHC PRB

A pilot-scale PRB containing 1%<sub>wt</sub> EHC injected across the width of a carbon tetrachloride (CT) plume effectively decreased the concentration of CT in groundwater at downgradient wells by 97% within 13 months, with no accumulation of degradation products (Biteman et al., 2007). The CT plume extends from a grain elevator approximately 2,500 feet (760 meters) downgradient where it discharges into a small creek; the highest concentrations of CT (2,500 ug/L) are located near the source area. Chloroform (CF), chloromethane, and methylene chloride have also been identified in study area groundwater.



**Figure 5. Concentration of CT in monitoring wells located upgradient and downgradient of the PRB.**

Groundwater sampling results as early as four months after installation of the PRB showed a 76% and 88% decline in CT concentration at monitoring wells located 70 and 140 feet (21 and 43 meters) downgradient of the PRB, respectively. Groundwater sampling results 13 to 22 months after installation of the PRB showed a 97% decline in CT concentration 70 feet (21 meters) downgradient of the PRB. Groundwater sampling results 22 months after installation of the PRB have showed approximately a 90% decline in CT concentration 600 feet (183 meters) downgradient of the PRB. No significant accumulation of chlorinated intermediates has been observed at any sample point. These results have remained consistent over a cumulative 42 months of post-construction monitoring.

#### **4.0 Summary**

Theoretical considerations and bench-scale study results suggest that a predicted longevity of EHC treatment materials in the field of three to five years is reasonable, and may even be an underestimate. Field data have shown longevity of over three years. Certainly there are many factors that can influence the actual longevity observed at a given site. Factors such as temperature, groundwater flow velocity, electron acceptor demand, mass applied, installation method, and inorganic chemistry are just a few of the factors that could affect the actual longevity. However, it appears that longevity of 5 years for EHC may be achievable in most subsurface environments.

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