ADVENTUS
Proven Soil, Sediment, and Groundwater Remediation Technologies

EHC for Chloropropanes

Technology Overview –

EHC® ISCR™ Technology for Chloropropanes

EHC®
The Original Injectable ISCR Reagent for Groundwater Applications

Understanding the Problem

Chloropropanes are industrial chemicals that have been used as solvents, dry cleaning fluids, paint removers, metal degreasers, and for the synthesis of bulk chemicals such as pesticides, resins, dyes, adhesives, plasticizers and surfactants (van Agteren *et al*., 1998). 1,2-Dichloropropane (Propylene Dichloride; 1,2-DCP) has been used to prepare soil fumigants for nematodes and insecticides for stored grain (EPA, 2006). Releases of chloropropanes to the environment have occurred due to agricultural use, industrial emissions and disposal, and volatilization during use (van Agteren *et al*., 1998). Application of pesticides to soil has also resulted in groundwater contamination at many Sites (van Agteren *et al.*, 1998). The EPA established a Maximum Contaminant level (MCL) of 5 ug/L (ppb) 1,2-DCP in drinking water.

Overview of EHC Technology

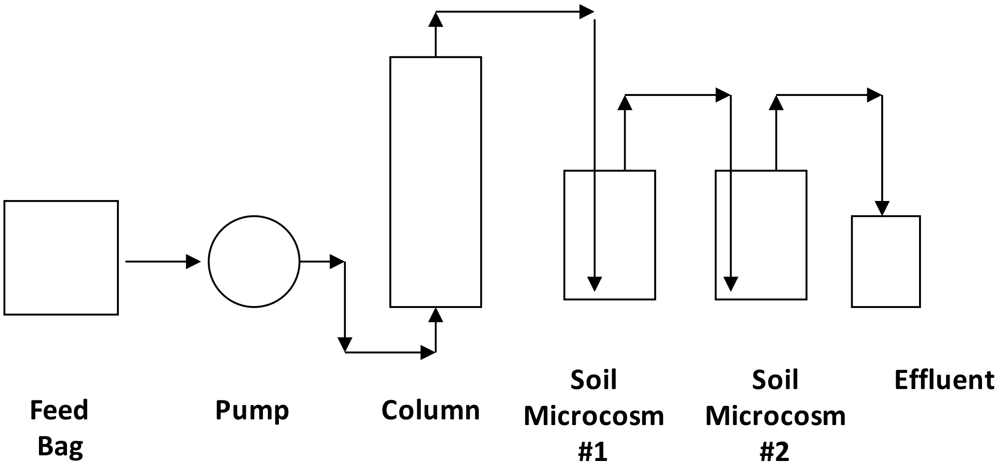
EHC® is the <u>original</u>, patented combination of controlled-release carbon and zero valent iron (ZVI) particles used for stimulating *in situ* chemical reduction (ISCR) of otherwise persistent organic compounds in groundwater. Variations of these materials have been used to treat over 8,000,000 tons of soil/sediment impacted by recalcitrant compounds as part of the company's DARAMEND® bioremediation technology. Both EHC and DARAMEND are proven, established technologies that have been used at hundreds of sites throughout the world. The technologies have been accepted by many Federal, State, and regional regulatory authorities.

For *in situ* applications, aqueous slurry of EHC is typically injected into the subsurface using a number of available technologies, including direct injection through GeoProbe rods and hydraulic/pneumatic fracturing. The EHC slurry may also be applied via direct application into trenches or by using deep soil mixing equipment. Common applications include hot-spot treatment, plume treatment and plume management using a permeable reactive barrier.

Laboratory Studies - Treatment of 1,2-Dichloropropane

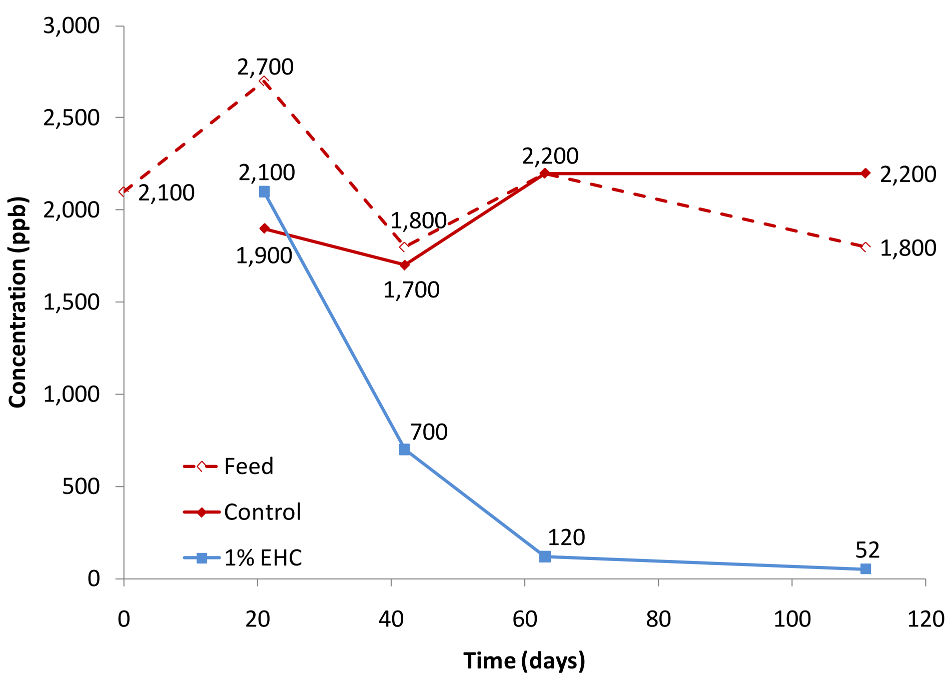
Adventus conducted bench-scale treatability studies using groundwater from a Site containing 2,100 µg/L 1,2-DCP and trace concentrations (38 µg/L) of organochlorine pesticides (OCPs). The experimental system consisted of a column followed by two downstream microcosms (**Figure 1**). The EHC column contained Site soil and was amended with 1% EHC (based on mass of soil in the column). The first downstream microcosm contained concrete sand and was also amended with 1% EHC. The second microcosm of the EHC systems contained only sand to assess contaminant removal downstream of the EHC zone. The column and sand microcosms of the control system were loaded as described above for the EHC system except no EHC was added. Clean sand, instead of Site soil, was used in the downgradient microcosms to avoid a potential interference from chloropropanes and OCPs desorbing from the impacted Site soil.

Figure 1: Schematic of experimental system



The EHC system supported treatment of 1,2-DCP during all four sampling events (**Figure 2**). On Day 111 (the final sampling event), the 1,2-DCP concentration was reduced from 1,800 µg/L in the feed to 55 µg/L in the EHC column effluent. This corresponded to a 97% reduction in 1,2-DCP.

Figure 2: Influence of EHC on groundwater 1,2-Dichloropropane concentrations



Field Application – Confidential Site, Western USA

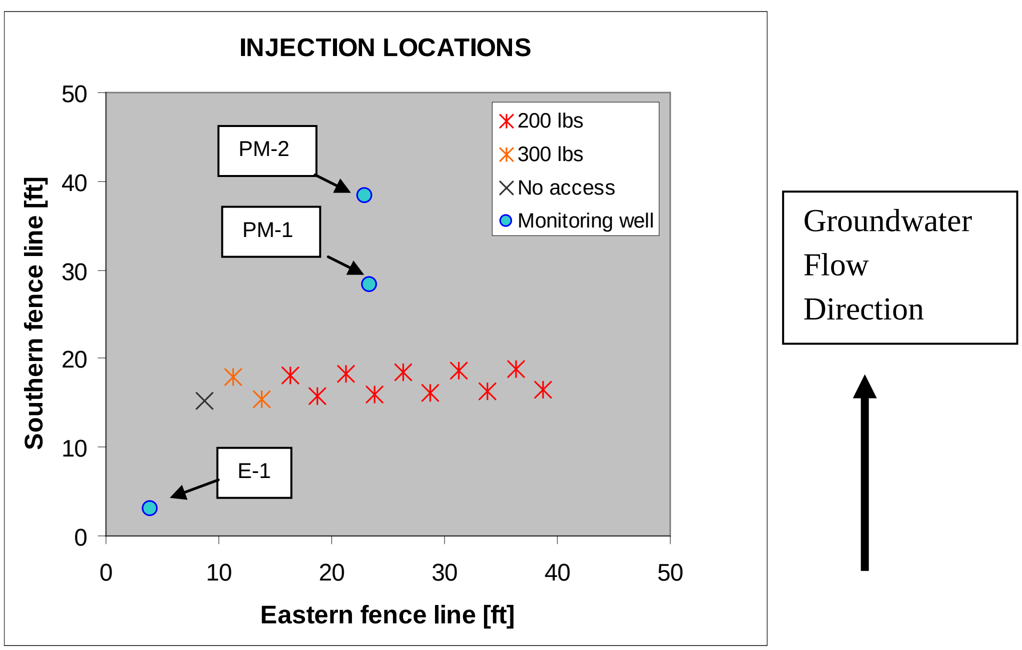
Site groundwater contained elevated concentrations of nitrate-nitrogen, ammonia-nitrogen, ethylene dibromide, 1,2,3-trichloropropane, and 1,2-dichloropropane (**Table 1)**. The targeted treatment zone was from 60 to 80 ft bgs. A field scale engineering optimization study was conducted to: 1) evaluate the effectiveness of the proposed subsurface injection method, and 2) validate the performance of the EHC ISCR technology under field conditions.

Table 1: Baseline concentrations (October, 2004).

Constituent of Interest (COI)	Concentration
nitrate-nitrogen	2,000 ppm
ammonia-nitrogen	700 ppm
sulfate	1,700 ppm
ethylene dibromide	50 ppb
1,2,3-trichloropropane	130 ppb
1,2-dichloropropane	1,400 ppb

In October 2006, EHC (2,600 lbs) was injected to create a permeable reactive barrier (PRB) measuring approximately 30 ft long x 8 ft wide x 20 ft deep (from 60 to 80 ft bgs). This resulted in an average application rate of 0.5% EHC to soil mass within the PRB at a product cost of \$8.7 per ft^2 of PRB cross section. The EHC was injected into two rows, spaced 2.5 ft apart and off-set by 2.5 ft. Between 200 and 300 lbs of EHC was injected into each of 12 injection points (**Figure 3)**.

Figure 3: Layout of EHC injection locations and mass of EHC injected per location.



CVOCs. Performance monitoring was conducted using data from monitoring wells located upgradient and downgradient (10 and 20 ft downgradient) of the PRB (**Figure 3**). Observed removal rates have been up to 61 and 67% for 1,2-DCP and 1,2,3-TCP respectively 10 ft downgradient from the PRB (**Figure 4**). Similar reductions were developing 20 ft downgradient (**Figure 5**). Meanwhile, inflowing concentrations have increased throughout the study (**Figure 6**).

Figure 4: Effect of EHC PRB measured 10 ft downgradient from injection zone (PM-1).

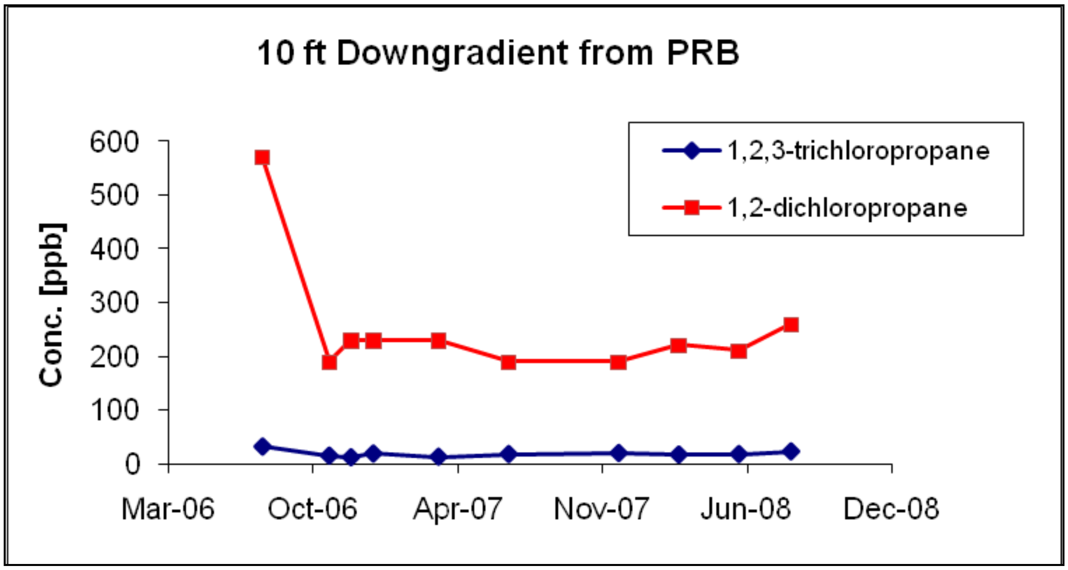


Figure 5: Effect of EHC PRB measured 20 ft downgradient from injection zone (PM-2).

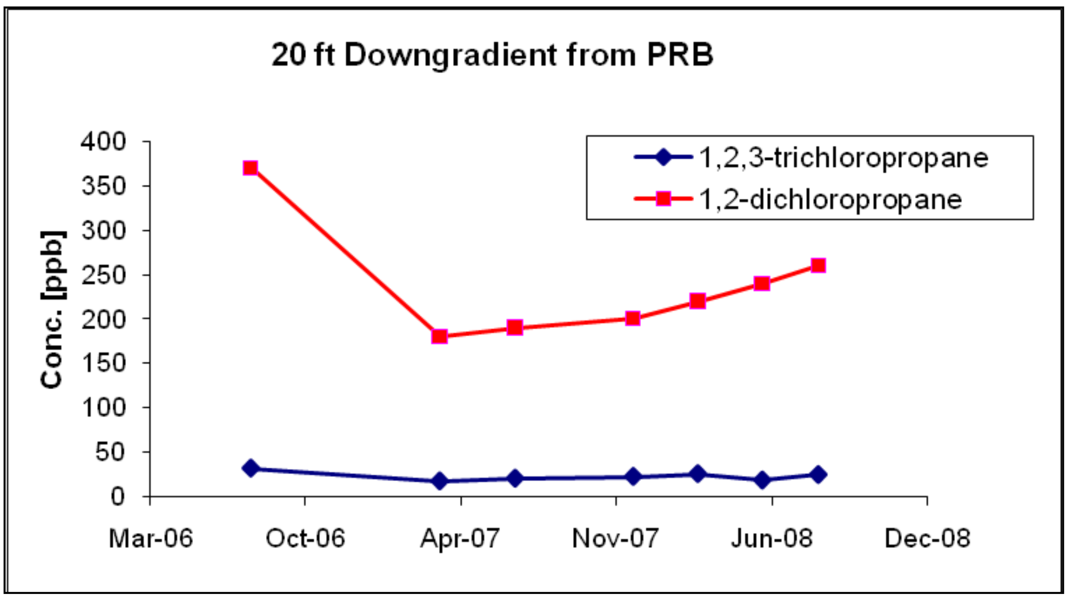
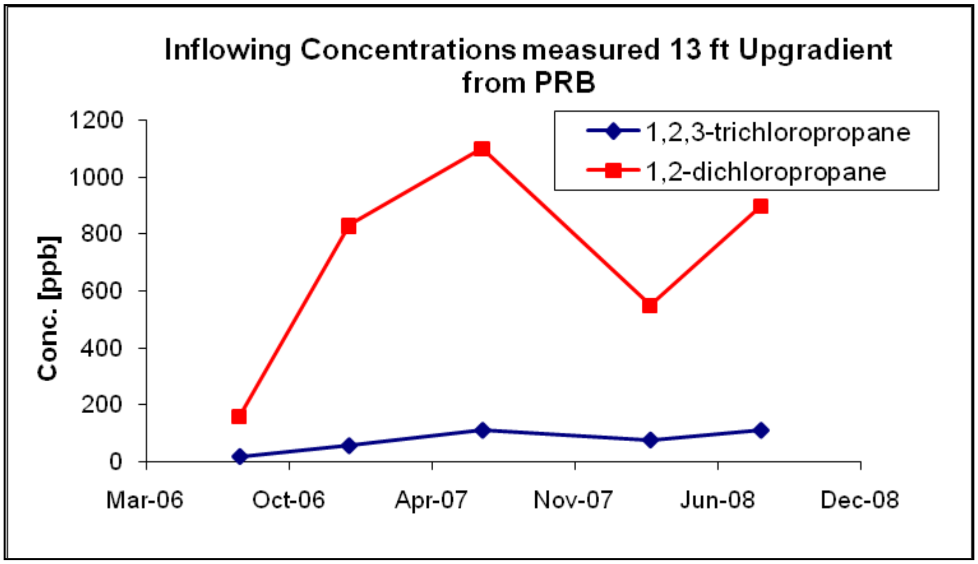
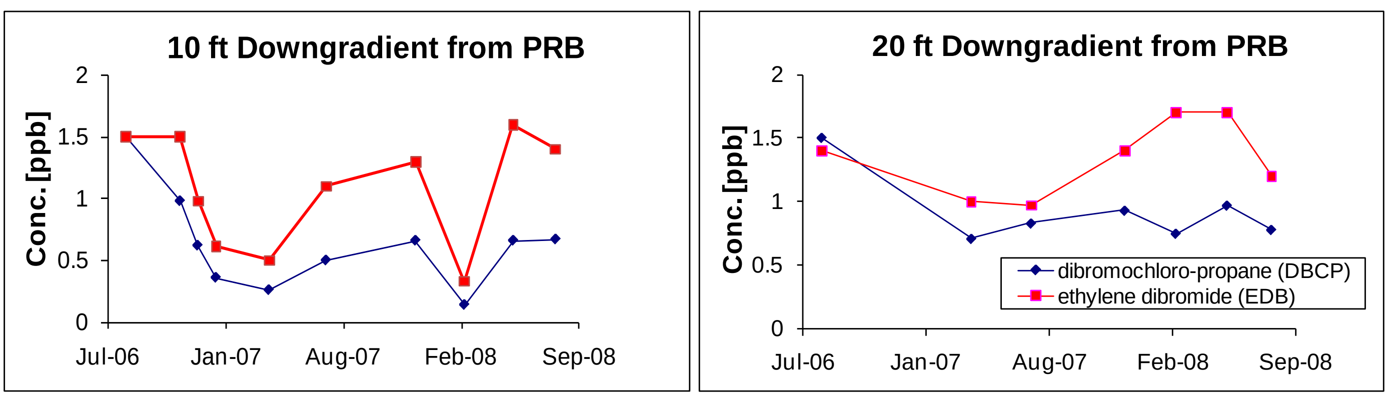


Figure 6: Inflowing concentrations measured ca 13 ft upgradient from injection zone.



Fumigants: Removal of DBCP has been up to 83%, 10 ft downgradient from the PRB. The concentrations of EDB have fluctuated at both downgradient monitoring wells hence there are no clear trends (**Figure 7**). The analysis is complicated by heavily varying inflowing concentrations, which have increased from a baseline concentration of 0.67 ppb to 4.4 ppb at the upgradient monitoring well Concentrations measured downgradient from the PRB is hence approximately 4-times lower than the most recent inflowing concentrations, but in line with baseline values measured before the installation of the EHC PRB.

Figure 7: Effect of EHC PRB on DBCP and EDB.

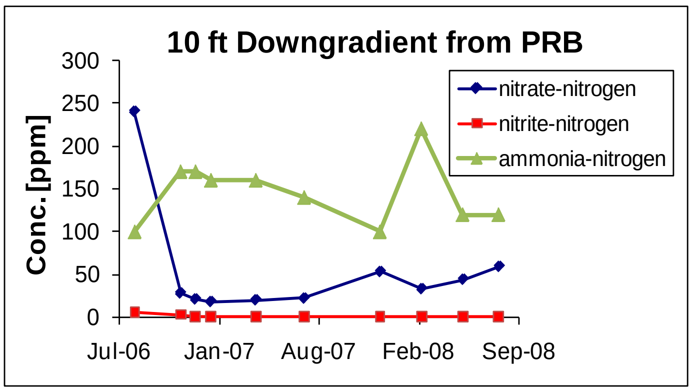


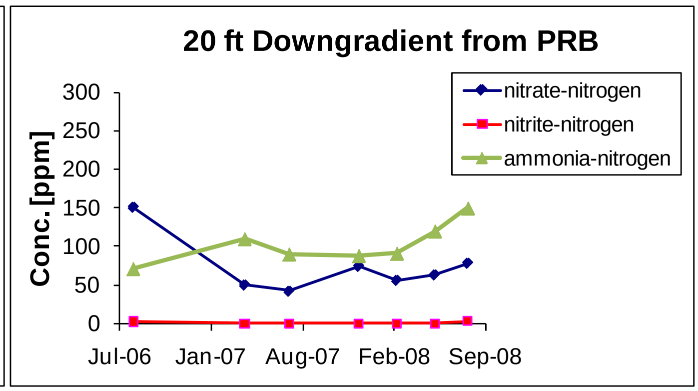
Nitrate: EHC promotes denitrification of nitrate and nitrite by providing bioavailable carbon (shown here as CH_2O):

$$4NO_3^- + 5CH_2O \rightarrow 2N_2 + 5HCO_3^- + H^+ + 2H_2O$$

Concentrations of nitrate and nitrite have remained below initial values since the first post-injection sampling event conducted in November 2006 (**Figure 8**). Observed removal rates have been up to 92 and >98% for nitrate and nitrite respectively 10 ft downgradient from the PRB. An overall decrease in nitrogen suggests that we have denitrification going on (conversion of nitrate to nitrogen gas). A smaller increase in ammonia suggests that reduction of nitrate back into ammonia may be occurring as well. This could be expected to occur under sulfate-reducing/methanogenic conditions. However, inflowing concentrations of ammonia have also steadily and significantly increased throughout the study from a baseline concentration of 21 ppm to 1,500 ppm measured at the upgradient monitoring well. Thus, the slight increase of ammonia measured at downgradient wells may therefore be due to an increase in inflowing concentrations.

Figure 8: Effect of EHC PRB on Nitrogen Compounds.





Conclusions

EHC product cost was \$8.7 per ft^2 of PRB cross section. With an estimated life of >60 months, continued monitoring is expected to show that *in situ* chemical reduction using the EHC technology offers a safe, effective and cost-efficient remedial solution for similarly impacted environments.

References

van Agteren, Martin H., Sytze Keuning, Dick B. Janssen. 1998. Handbook on Biodegradation and Biological Treatment of Hazardous Organic Compounds. Kluwer Academic Publishers, Netherlands. Page 127.

US EPA. 2006. http://www.epa.gov/safewater/contaminants/dw_contamfs/12-dich3.html (November, 2006)