

## Considerations for Planning an *In Situ* Injection Project

### - An open, honest review of lessons learned from remediation challenges -

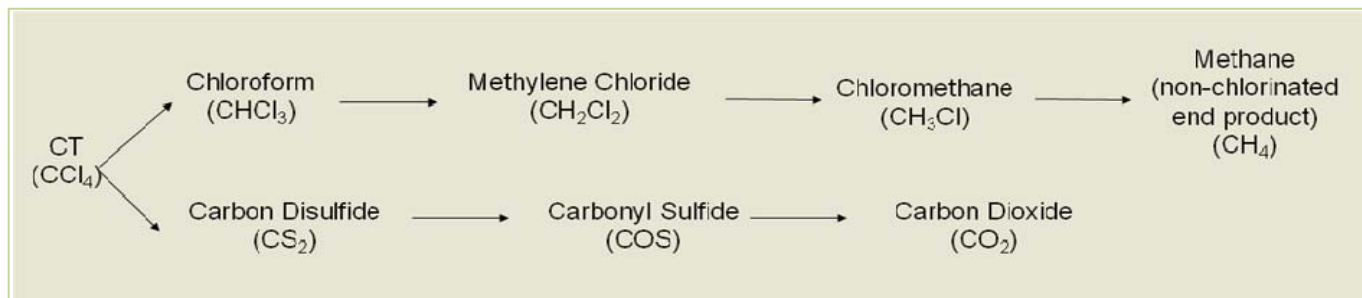
Professional and experienced remedial practitioners acknowledge that some of their remediation projects have met formidable challenges – we admit the same. Regardless of time or budget, it is sometimes difficult to plan for every aspect of an *in situ* remediation project. We all know that prior to implementing an *in situ* remedy a thorough understanding of site-specific factors such as biogeochemical conditions and lithological features can significantly increase the chances of success. However, a number of other features are sometimes overlooked resulting in unexpected, undesirable secondary issues such as mobilization of arsenic, aquifer acidification, accumulation of dead-end intermediates, plume dispersion, *etcetera*.

This summary presents some of the lessons learned from hundreds of field sites around the world where we have applied EHC™ *In Situ* Chemical Reduction (ISCR™) technology. We provide an overview of some relevant factors in potentially troubling *in situ* injection scenarios, including (transient) observation of compounds related to microbial fermentation (e.g., acetone and MEK), unexpected daughter products of CVOC degradation, mobilization of metals sorbed to or present in the soil matrix, CVOC concentration spikes after an injection, and daylighting/short-circuiting during injection. These potential problems are followed by open communications on how they can be forestalled and potentially managed.

### Unexpected Transient Catabolites from CVOC Degradation

Major catabolites typically generated from reductive dehalogenation and *beta*-elimination reactions are usually anticipated and monitored. However, we occasionally encounter other catabolites – albeit at low concentrations – that are generated via less common pathways. For example,

- We observed carbon disulfide (CS<sub>2</sub>) at a site in Midwest USA where EHC was used to treat groundwater containing up to 4,000 ppb Carbon Tetrachloride (CT). A peak concentration of 79 µg/L CS<sub>2</sub> was observed soon after EHC injections; however the CS<sub>2</sub> concentrations quickly tapered off a few months after injections, and they have remained below criteria (generally not detected) for about 3 years. CS<sub>2</sub> has been shown to form in some cases during reductive dechlorination of carbon tetrachloride during the sulfate reduction phase (Devlin and Muller, 1999).



- The formation of lower concentrations of chlorinated ethanes (DCA and CA) has been observed at two sites in the Northwest USA where EHC was injected to treat chlorinated ethenes (PCE/TCE/DCE). While the chlorinated ethanes formed made up no more than approximately 1% of the starting CVOC concentrations, in both of these instances the concentrations of DCA and CA temporarily exceeded

MCLs before being further degraded to ethane. The pathway of formation is hypothesized to be hydrogenation of DCE or VC to form DCA or CA, respectively (*i.e.*, addition of two hydrogen atoms and converting the carbon double bond to a single bond) as previously suggested by others (Barrio-Lage, *et al.*, 1986; Sims *et al.*, 1990). Alternatively, these may be abiotic reactions co-catalyzed by the presence of other reactive metals indigenous to the site (*e.g.*, nickel, palladium). It is also possible that these compounds represent other biogeochemical reactions that have yet to be fully elucidated (Brown *et al.*, 2009).

### **Transient Production of Acetone and MEK from Fermentable Carbon Sources**

When observed, production of MEK (*i.e.*, 2-butanone) and acetone seem to occur simultaneously. We have developed several general hypotheses:

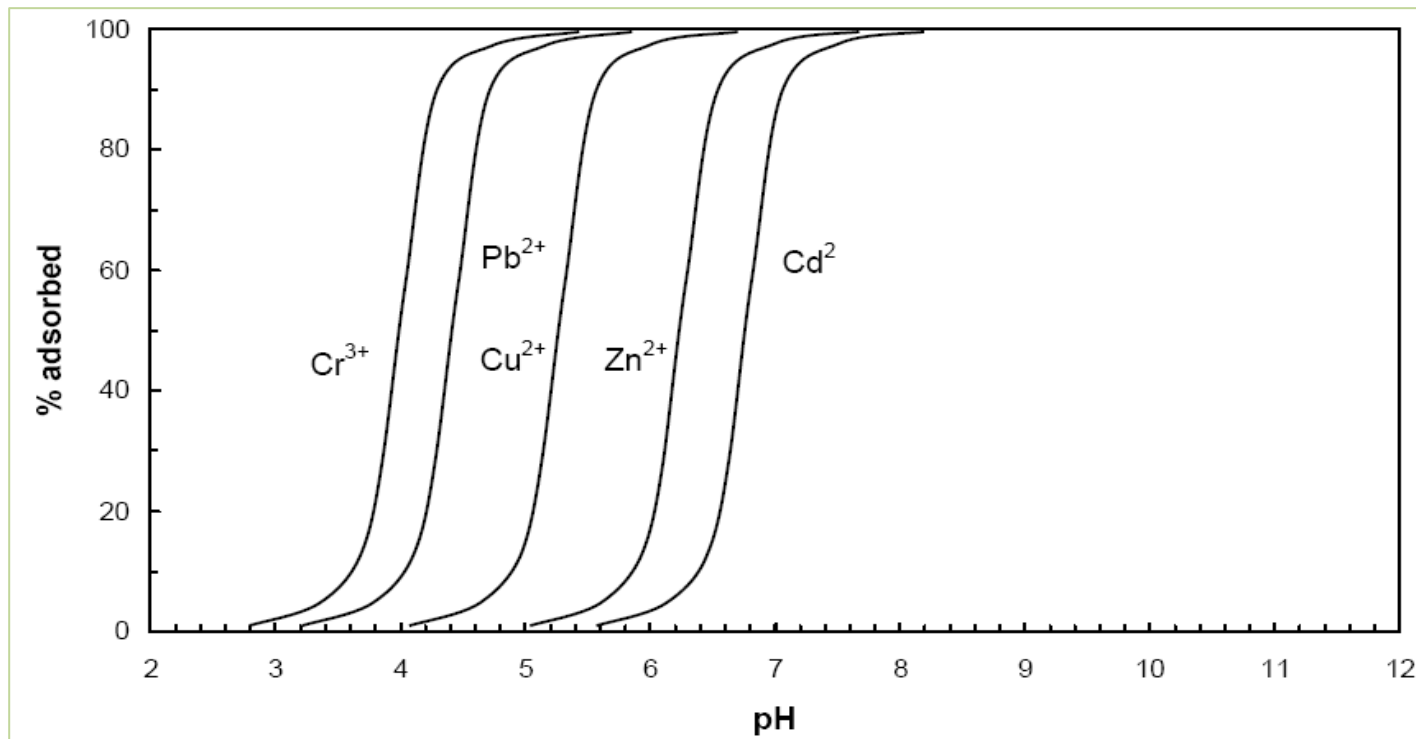
1. Lab artifacts. Despite the obvious, VFAs such as propionic acid can be biologically reduced to isopropyl alcohol (IPA). IPA undergoes photocatalytic oxidation to acetone. This photocatalytic oxidation can occur during the sample hold time (between sample collection and analysis).
2. False Positives - Certain VFAs may be transformed into acetone during sample preservation and/or analytical processing. Knowing that EHC (and some other sources of carbon) will generate large volumes of VFAs, this is a possibility to consider: *i.e.*, “acetone” is reflective of high VFAs. For example, it is possible to convert acetic acid or other VFAs to acetone by high temperature and the packing in a column during GC analysis. It may even be possible to make this conversion during certain sample clean-up steps that are employed prior to GC analysis. There is also some evidence that certain metal oxides can convert acetic acid into acetone: some aquifers have a lot of native iron oxides.
3. Contaminant from field activities: Materials are residuals from cleaning equipment, *etcetera*.
4. Microbial production of acetone/MEK. Recognized pathways for anaerobic biodegradation of TCE do not include acetone/MEK as major intermediates (<http://umbbd.msi.umn.edu/index.html>). However, fermentation of organic carbon can result in the production of MEK and acetone (<http://www.navylabs.navy.mil/Archive/emdq-2005/2-3-1.pdf>). Field data showing occasional, transient presence of acetone/MEK seem to occur most often when alkanes are present along with high organic carbon, methanogens, and hypoxic environments. It can therefore be assumed that acetone/MEK production occurs before the aquifer system goes fully anaerobic, or soon after initial introduction of a carbon source. In all cases where EHC has been applied the production of acetone/MEK has been a transient, short-lived phenomenon.
5. Minor Catabolites of ZVI Reactions. At some sites where acetone/MEK have been a concern (above guidelines) following EHC injections the concentrations have been beyond what could be easily explained as a by-product of TCE degradation. In iron literature, there are reports for small amounts of butane (C<sub>4</sub>H<sub>10</sub>) and butene (C<sub>4</sub>H<sub>8</sub>) formed from TCE and TCA. Oxidation from butane to MEK could also occur.

In summary, if you are observing acetone/MEK following a biologically based remedial action this may be related to the high VFAs resulting from carbon fermentation. The amount of acetone/MEK produced will likely be influenced by the amount and type of carbon used and the site specific microbial processes. If EHC was employed the production of these compounds will rapidly decline with time. It should also be noted that both acetone and MEK rapidly attenuate in the down gradient, aerobic zones.

### Mobilization of Arsenic and Other Metals

With any *in situ* treatment approach the aquifer biogeochemistry is altered and there is a risk of mobilizing metals sorbed to, or present in, the aquifer matrix. For example, reductive anaerobic dechlorination is effective in reducing chlorinated solvent concentrations in groundwater, but may result in a release of metals bound within iron oxides, manganese oxides or other clay minerals in the aquifer material. This process may occur via reductive dissolution or desorption from those mineral phases, as a result of changes to pH and redox potentials. Examples of such metals include As, Se, Fe and Mn (AFCEE, 2004).

Notably, EHC maintains a near-neutral pH, as the acidity of carbon substrate degradation is offset by the alkalinity resulting from zero-valent iron (ZVI) corrosion. This minimizes some of the metals dissolution effects relative to carbon-only substrates. One mechanism for such metals to be sequestered through the use of EHC is the complexation with hydrous ferric oxides (HFOs). **Figure 1** shows some sorption rates for various metals on HFOs. Naturally, the presence of ZVI in EHC enables this mechanism through a continuous generation of iron oxides and oxyhydroxides from the corrosion of ZVI particles. For sites where mobilization of metals cations is of specific concern, our EHC-M™ formulation includes a source of sulfur to promote precipitation as metals sulfides. It is therefore recommended to consider the potential for metals mobilization beforehand and measure natural sulfate levels to evaluate the need for EHC-M.

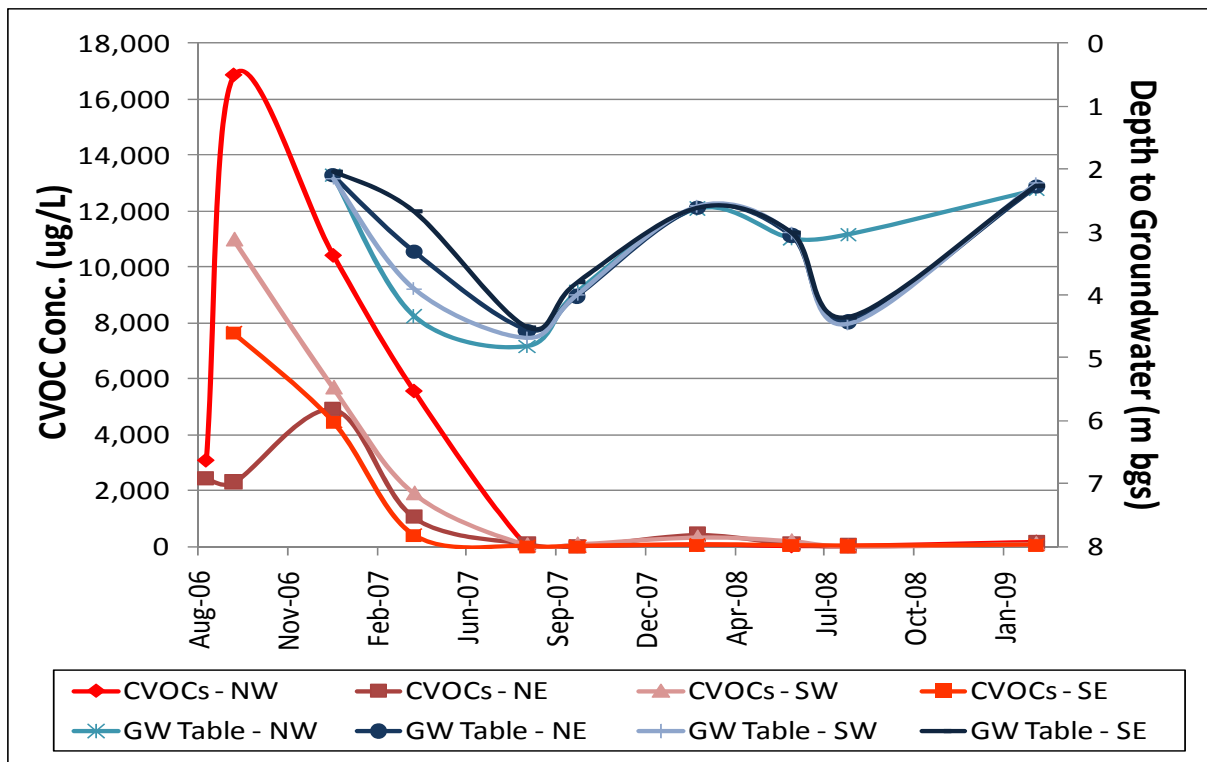


**Figure 1:** pH dependent sorption rates on HFOs.

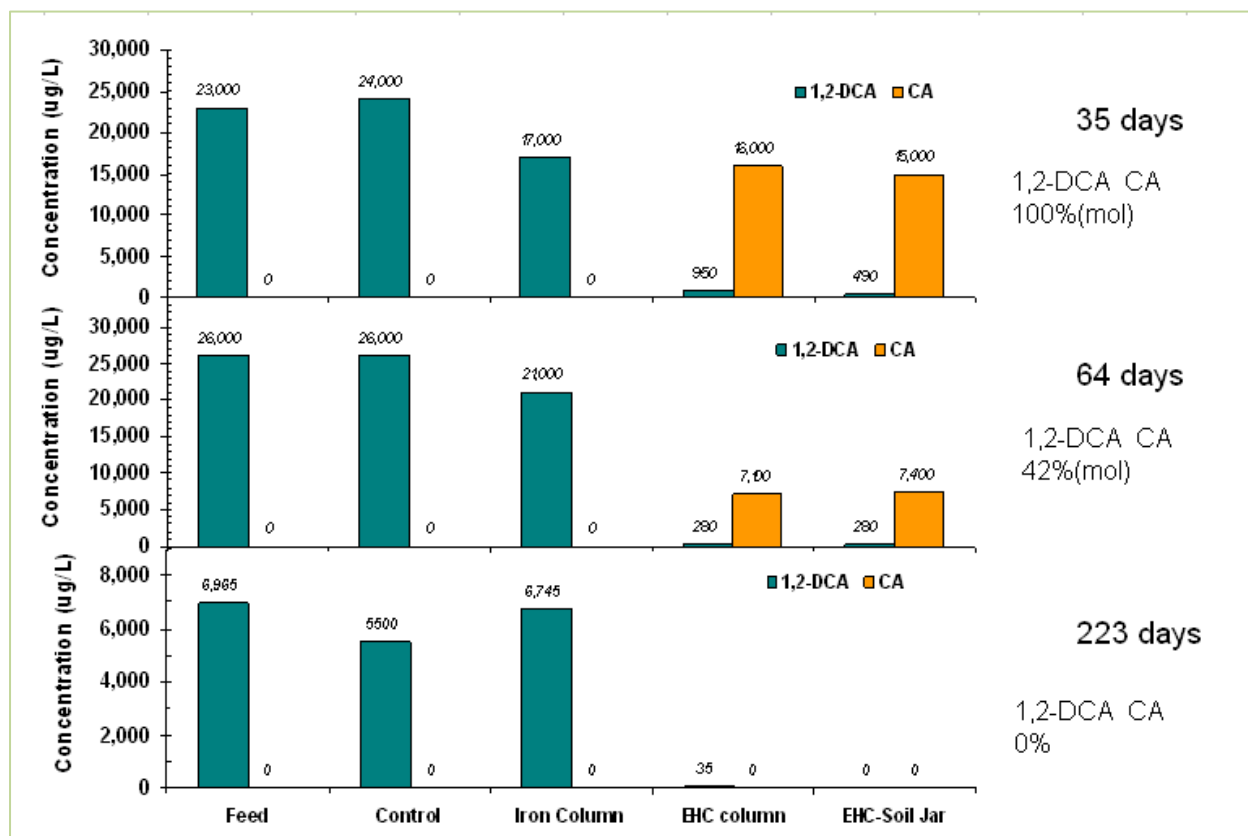
### COI Concentration Spikes after Injection

Transient spikes in COI concentration sometimes occur immediately following injection of amendments. This can result from a number of sources. **Figure 2** shows data from one of our EHC sites, where seasonal groundwater table fluctuations resulted in flushing of compounds from the smear zone. Other factors that can result in concentration changes include:

- Dissolution of residual NAPL/ganglia, if present, can cause concentration spikes.
- Pore volume (PV) displacement - Depending on injectate volume, chase water requirements and aquifer porosity water table increases may occur during injection thereby flushing/mobilizing compounds from unsaturated soils. Conversely, this may also cause artificial concentrations drops if plume displacement is occurring. These problems are more typically observed with emulsified oils since they require higher injection volumes and chase water. To date we have not observed water table increases with EHC, as we typically only displace 2 to 10% of the aquifer PV.
- Compound degradation chemistry – Increases in daughter products of many organic compounds can be observed immediately following an injection before low redox conditions are established. EHC is unique and superior in its ability to taking these reactions to completion after low redox conditions are established, as shown in **Figure 3**.



**Figure 2:** Total CVOC concentrations and depth to groundwater measured at four wells within an EHC treatment area. A general increase in the CVOC concentrations was observed during the first two post-injection monitoring events, conducted in September 2006 and January 2007. However, historical and background data suggests that this increase was related to introduction of CVOCs from the smear zone in relation to an increase in the water table. Subsequent sampling events showed smaller rebounds during the rainy season (high groundwater table).



**Figure 3:** Effect of ISCR (*i.e.*, EHC) on 1,2-DCA and CA in groundwater measured under flow-through laboratory test conditions. Treatment performance improved and daughter production reduced to zero with time, as ISCR reducing conditions were established.

### Daylighting and Short-Circuiting

“Daylighting” is a term commonly used to describe the surfacing of injectate. This can occur when injecting any type of amendment under pressure and must be anticipated during an injection job. Our preferred contractors have found the following to be helpful in minimizing potential daylighting:

- Minimize injected volume – with EHC, typical source area injection volumes of 2 to 10% of PV are used. In some PRB (non-source area) installations, a maximum of 20% of PV is displaced. Many other injectates require significantly more PV displacement.
- Reduce pressure and flow-rate – this is site-specific, but the lowest pressure for a sustainable low-flow rate (< 10 gpm) seems generally best.
- Ideal borehole abandonment – slurry grouts do not always work well unless sufficient time is allowed for set-up. In our experience, it is best to employ some form of bentonite pellets, such as HoleBlok+ (<http://www.adventusgroup.com/products/holeblok.shtml>). If historical boreholes were not properly abandoned, you may find this out during the injection process.

- Ideal viscosity – field experience shows that a slurry with ~30 wt% solids is generally optimum for injecting EHC and similar slurries. Again, site-specific results may vary and thicker slurries have been applied for shallow applications (from 2 ft bgs) to limit surfacing of slurry around the rods.
- Top-down vs. bottom-up injection protocol – use an injection tip that allows for flexibility in the field, for example Geoprobe’s pressure activated injection tooling.
- Allow pressure dissipation – Use of multiple rods and moving around the injection grid helps to enable localized subsurface pressures to dissipate.

In summary, plan for a flexible implementation and use an experienced remedial contractor prepared to work over a range of injection pressures, flow-rates, and installation approaches.

See <http://www.adventusgroup.com/contractors.shtml>



## References Cited

- AFCEE, 2004. Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents
- Barrio-Lage, G., F. Z. Parsons, R.S. Nassar and P.A. Lorenro. 1986. Sequential Dehalogenation of Chlorinated Ethenes *Environ. Sci. Technol.* 1986, vol. 20, pages 96-99.
- Brown, R.A., J. Mueller and A. Seech. 2009. Interactions between Biological and Abiotic Pathways in the Reduction of Chlorinated Solvents. Battelle's Tenth International *In Situ* and On-Site Bioremediation Symposium. May 5-8, 2009 Baltimore, MD USA.
- Devlin J.F. and Muller, D., 1999. Field and Laboratory Studies of Carbon Tetrachloride Transformation in a Sandy Aquifer under Sulfate Reducing Conditions, in *Environ. Science & Technology*, Vol. 33. Pages 1021-1027.
- Dzombak, D.A. and Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. New York: Wiley Science.
- <http://umbbd.msi.umn.edu/index.html>
- Sims, J.L., J.M. Suflita and H.H. Russell. 1991. Reductive Dehalogenation of Organic Contaminants in Soils and Ground Water. US EPA. EPA/540/4-90/054. January 1991.
- Vogel, T.M., C.S. Criddle and P.L. McCarty. 1987. Transformations of Halogenated Aliphatic Compounds. *Environ. Science & Technology*, Vol. 21. Pages 722-736.

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