Hydrogen Release Compound HRC®

Using HRC to Treat Residual Sorbed DNAPL Contamination

General Background

While it is clear that bioremediation is effective against dissolved phase contamination, which is readily available for microbial consumption, there has been debate about how easily a sorbed contaminant can be treated. First, we offer the following definitions of different types of DNAPL contamination, which will facilitate discussion.

DNAPL Contamination

Hydrophobic Sorption

This is generally a very low level of contamination that sorbs to clean aquifer materials after they are exposed to a dissolved phase plume. Typically the soil will superficially adsorb a few multiples of the dissolved phase concentration unless there is a significant amount of organic matter in the system. Under these high organic conditions there may be as much as one to two order of magnitude increase over the dissolved phase concentration, but this is still a fairly low level of total mass and is clearly the exception rather than the rule. The hydrophobic sorption value in most cases is between 1x and 2x the dissolved phase concentration. In our standard HRC Applications Software (see www.regenesis.com) we consider this factor as a function of the K_{OC} (organic carbon). The software relies on published data sets for hydrophobic sorption under a various conditions with K_{OC} being a major factor.

Residual DNAPL

When pure solvent enters the aquifer it sinks – hence the term DNAPL for Dense Non-aqueous Phase Liquid. As a result the liquid tends to "finger" through the aquifer forming "stringers" as well as droplets in its wake. A small amount of residual mass is of far greater impact than even a very high 100x hydrophobic sorption value. What we have here is "free product" but it exists in small amounts as droplets in the macropores or "stringers" that connect through several pores. This is a main target for HRC, beyond the dissolved phase and hydrophobically sorbed contamination. It is also the kind of contamination that new evidence shows we can effectively remediate by actively stimulating reductive dechlorination.

Free Phase DNAPL

This is "free product", a palpable amount of material that is usually only manageable by excavation, pumping or some other intensive mechanical process. HRC is generally

contraindicated in these settings – strictly from a stoichiometric perspective; there is just too much contaminant mass in free product for an affordable use of HRC. However, a final technology selection decision is still a function of the economic comparison to the next available solution for the problem as well as any special logistical constraints that would limit normal DNAPL removal operations.

In summary, at present we apply HRC without concern to all problems involving dissolved phase and hydrophobically sorbed contamination. The next challenge for us is to explore the limits of how we can affordably impact residual DNAPL and in rare instances the free phase contamination.

Treating Hydrophobically Sorbed and Residual Sorbed DNAPL

Why it Should Work

Microorganisms can accelerate sorbed contaminant removal by several mechanisms. Primarily, when microbes consume the "newly born" dissolved phase that is outside an actively desorbing source - they maintain a concentration gradient. In accordance with Fick's Law, the flux from the sorbed material will increase with the steepness of this gradient. Also, microbes may actively secrete "biosurfactants" which act like soap to facilitate desorbtion. Consequently, we have these two mechanisms for biological impact.

Experimental Evidence

Our work was modeled after the pioneering efforts of Dr. Joe Hughes at Rice University (Carr, C.S., Garg, S. and J.B. Hughes, 2000. The Effect of Dechlorinating Bacteria on the Longevity and Composition of PCE-Containing Non Aqueous Phase Liquids under Equilibrium Conditions. ES&T 34/6, 1088-1094).

In the studies we conducted we decided to focus on chlorinated solvents and the action of HRC on some or all of the phases we have discussed above. Three types of experiments were performed:

- The "Disappearing Drop Experiment"

A visible drop of TCE (about 0.5 grams) was placed in a flask. Water from a second flask containing soil and HRC was recirculated through the flask containing the pure TCE. The experimental set-up is shown in Figure 1. Figure 2 shows the results over 12 days in which the disappearance of the "free product" is clearly noted. The rate of removal is somewhat accelerated by the recirculation, which even though gentle is fast compared to typical aquifer flow. Still, even projecting these results out by a time factor of 10 to as high as 100, what is clearly illustrated is that small globules of DNAPL can be completely removed relatively quickly from the aquifer solely by microbial consumption

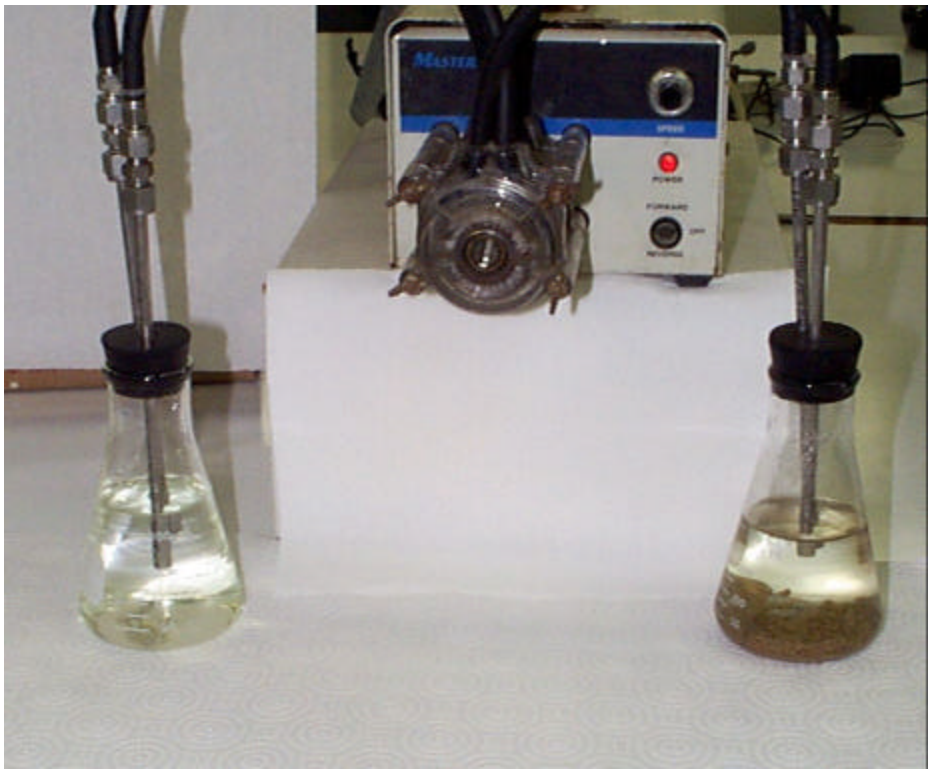

Figure 1. Experiment Set-Up

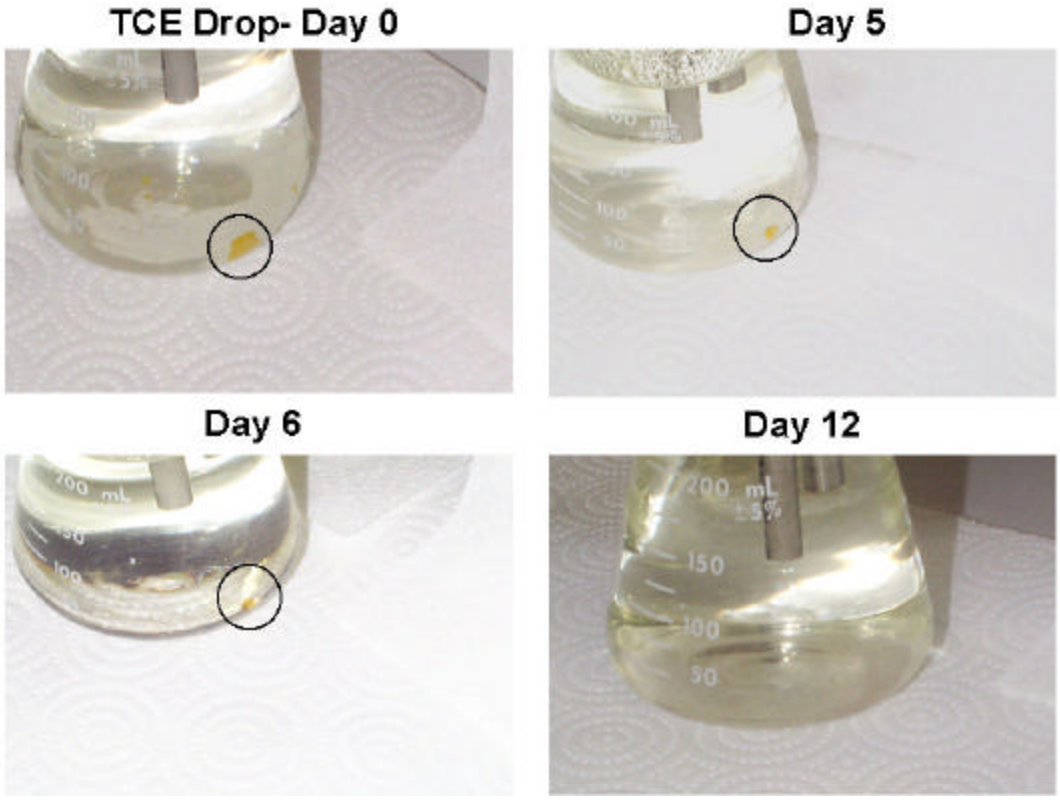

Figure 2. Disappearing Drop Results from Baseline to Day 12

- The "Hughes Experiment"

In a simple version of the experiment carried out in the paper cited above, a column of acclimated, microbially active soil was flushed with water saturated with TCE (175 mg/L) until the soil was saturated with TCE and in equilibrium with the dissolved phase. HRC was added to the soil and the aqueous phase circulating through the system was analyzed on a regular basis. The results are shown in Figure 3 and essentially represent the action of HRC on the dissolved phase and the soil bound hydrophobically sorbed material that replenishes the dissolved phase in accordance with Fick's Law.

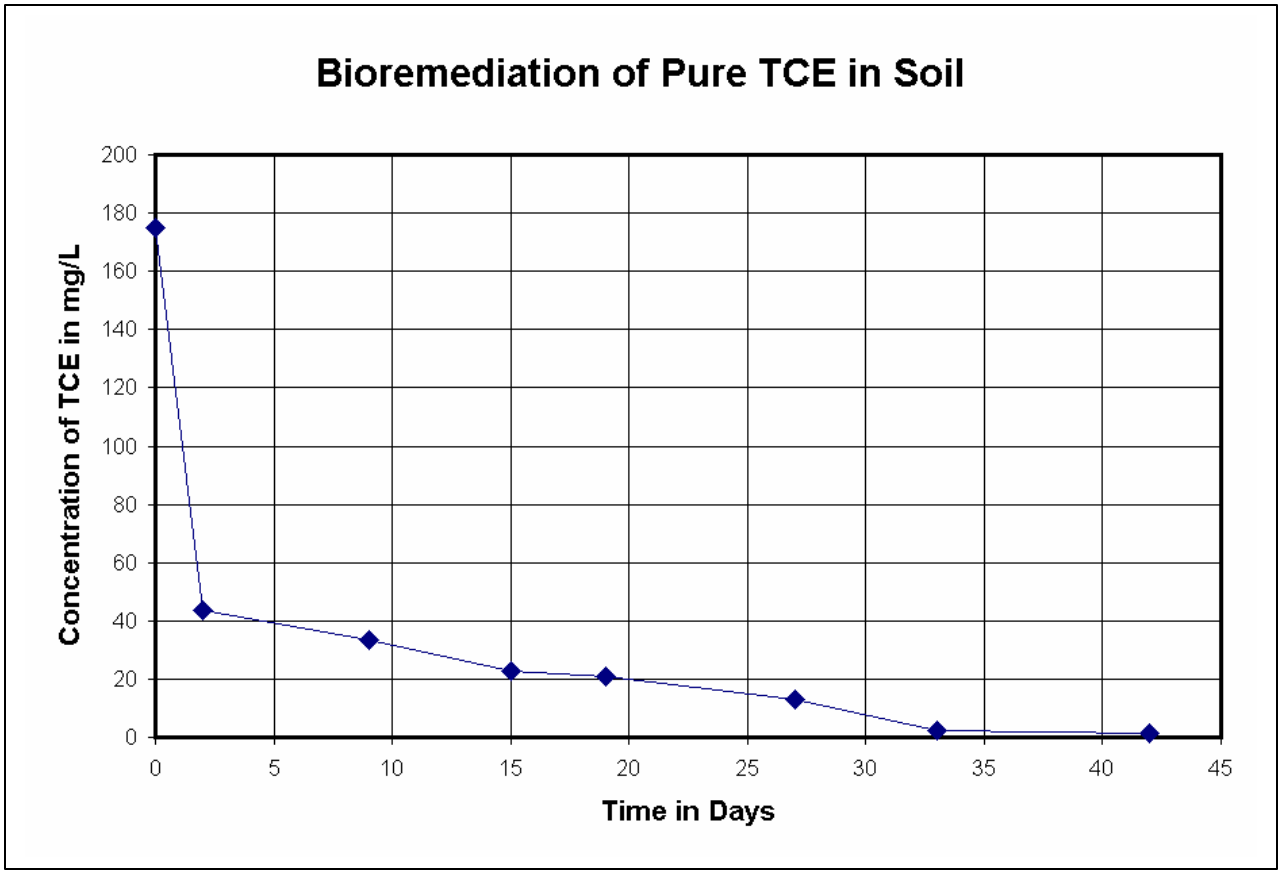

Figure 3. Hughes Experiment Results

- The "Modified Hughes Experiment" using higher initial DNAPL Mass

In this experiment replicate samples were created in which there was excess TCE. HRC was applied and the data was accumulated by complete analysis of a given set of tubes in a time series. In each test tube there was 10 grams of soil, 0.5 grams of TCE, 1.5 grams of HRC and 130 ml of distilled water. Figure 4 presents the change in total TCE mass in the system over time. Once again, what is clearly illustrated is that small globules of DNAPL can be completely removed relatively quickly from the aquifer solely by microbial consumption. Also, in contrast to the "Disappearing Drop" experiment, in which a moderate but artificially high flow was

present, in this instance the system was completely static and still there was a vary rapid removal of residual source under the direction of microbial action.

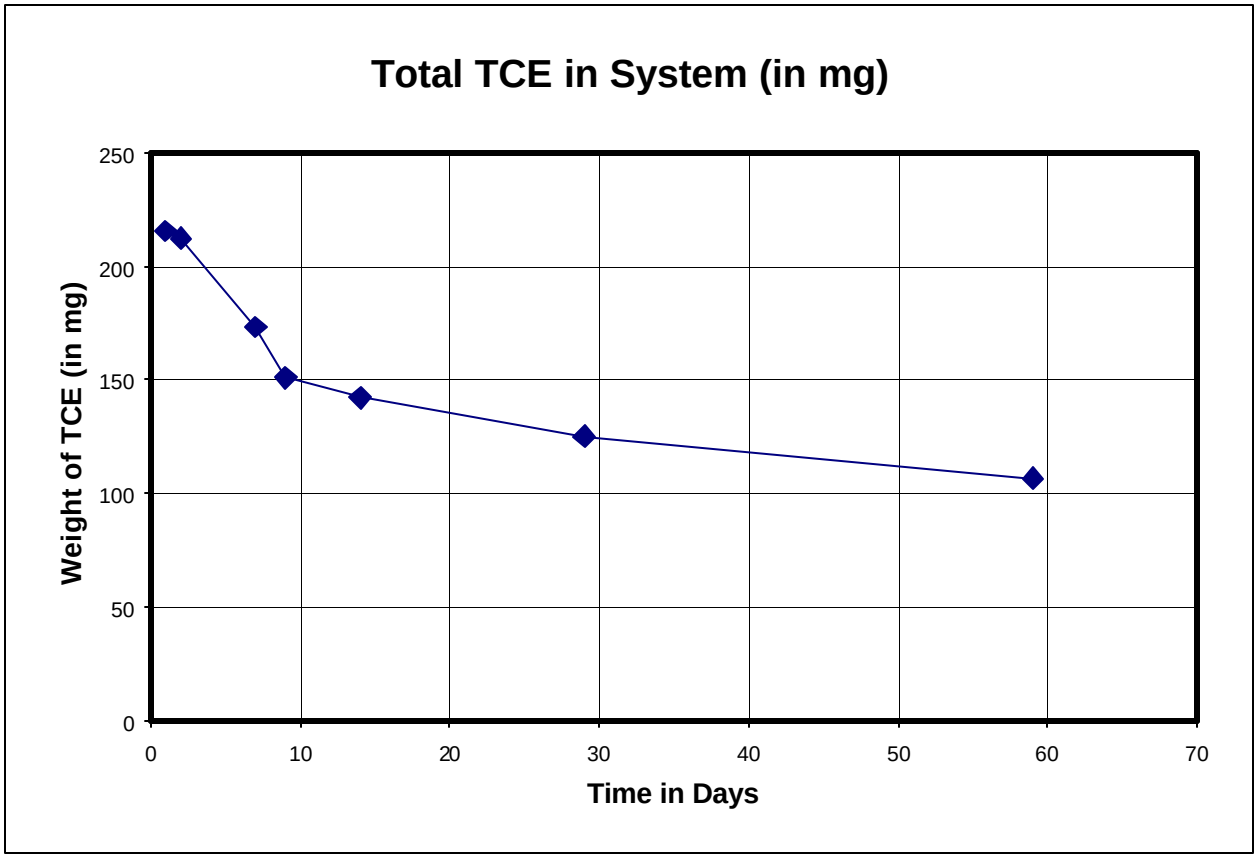

Figure 4. Results of the Modified Hughes Experiment

All of these experiments showed that the TCE was remediated very effectively. It was concluded that HRC can assist in the bioremediation of pure phase TCE either on or in soil whether in liquid form or adsorbed onto and into the soil.

Field Evidence

Proving that bioremediation accelerates desorption in the field is a daunting proposition due to the heterogeneity of the system, the costs and uncertainly involved. Still, Regenesis is examining some options and hopes to initiate such a project in the near future. In the meantime, there is some indirect evidence for bioremediation mediated in some of our field work to date.

If we consider a simple sequential dechlorination of TCE to the first daughter product DCE we can accumulate some indirect evidence for the desorption. Given that TCE degrades faster than DCE we can hypothesize that if desorption is occurring that we will see an excess of DCE in the system over time. So, as we get "turnovers" of dissolved phase TCE, where the dissolved phase is fed by desorption, the DCE levels systematically increase. Once again, the DCE build-up is a function of the kinetic disparity, i.e., the slower rate of removal of the DCE relative to the TCE.

This, in fact, is the case in several of our data sets and indicates we were treating an area with an unknown residual. This is not uncommon due to the fact that it is often hard to precisely locate a DNAPL source. As a result if we see a small reduction on TCE and a much larger increase in DCE in the same time period we are probably "turning over" the TCE pool by desorption. Two examples of this are presented as follows. The full studies are in the book entitled Accelerated Bioremediation of Chlorinated Compounds in Groundwater. Copies are available free of charge at our web site.

Case 1: Project Conducted by Haley & Aldrich

A site in New York was contaminated with TCE at concentrations reaching 26,000 ug/L in a very tight glacial till and clay aquifer with a very low velocity (hydraulic conductivity = 0.01 ft/day). Depth to groundwater was recorded at approximately 5 ft bgs. Approximately 500 lb of HRC were injected into borings spaced 5 ft on center in a 560 ft^2 grid.

Figure 5 clearly shows that the DCE daughter product appears in excess of the TCE parent material over time. Also, the data is particularly valid because it expresses total mass in the system as a function of a kreiging modeling exercise that can determine the mass from a collection of individual well measurements. In the initial time period from Day 0 to Day 89 there is a decrease in total TCE mass from 625g to 477g – a difference of 148 g, yet there was an increase in DCE from 43 to 430 g for a net gain of 387 g. Looking at it on a more accurate molar basis, 1.12 moles of TCE were removed and 3.99 moles of DCE were formed which is a difference of about 3.5 X!

Between Day 89 and Day 166 we see a fairly robust reduction of both constituents, but then again beginning at Day 166 through to Day 461 there are clear build-ups of DCE in a background of a minimally variable TCE change. As another case in point, from Day 166 to Day 273 we see a mass increase of 226 g of DCE for a loss of only 3 g of TCE. Again on a molar basis 2.33 moles of DCE formed from an apparent loss of 0.02 moles of TCE – a 100-fold difference. We believe that these discrepancies reflect the fact that TCE is being replenished through desorption as it is remediated and forming the less reactive DCE.

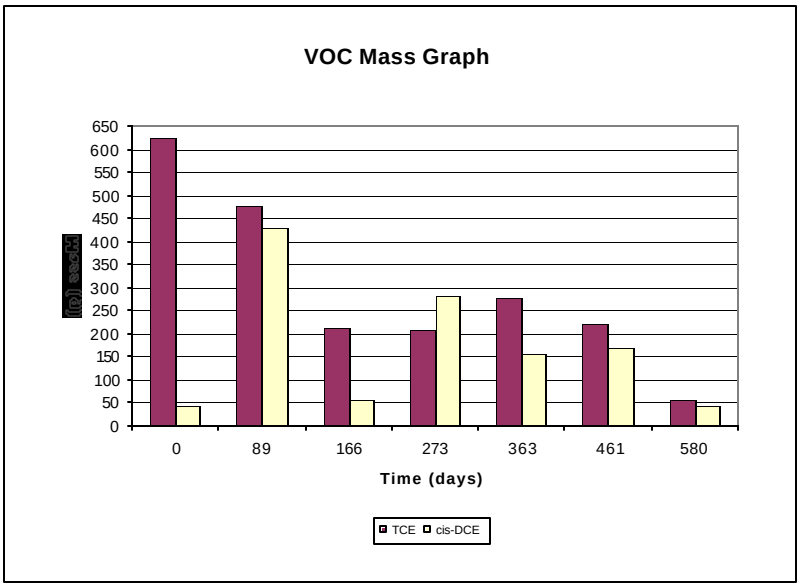

Figure 5. Haley & Aldrich Mass Graph

Case 2: Project Conducted by Harding Lawson

A site in Kansas was contaminated with PCE at concentrations reaching 7,000 ug/L in a silt and clay aquifer with a groundwater velocity of approximately 0.03 ft/day. Depth to groundwater ranges from 5 to 9 ft bgs. HRC was applied to the area using 15 injection points.

Figure 6, displaying the results from a single downgradient sentinel well, clearly shows that the DCE daughter product appears in excess of the PCE parent material over time. From day 0 to day 27, we see PCE concentrations decrease from 6,500 ug/L to 210 ug/L (97%). Past day 27, PCE levels remain stable. TCE decreases from 840 ug/L at day 0 to 540 ug/L at day 118. DCE rises from a baseline concentration of 560 ug/L to a final concentration of 15,000 ug/L at day 118. Translating this into moles, the removal of 38 moles of PCE and 2 moles of TCE produced 149 mol/L of DCE. The 3.8x differential of DCE mass could be attributed to a desorbtive turnover of PCE and TCE.

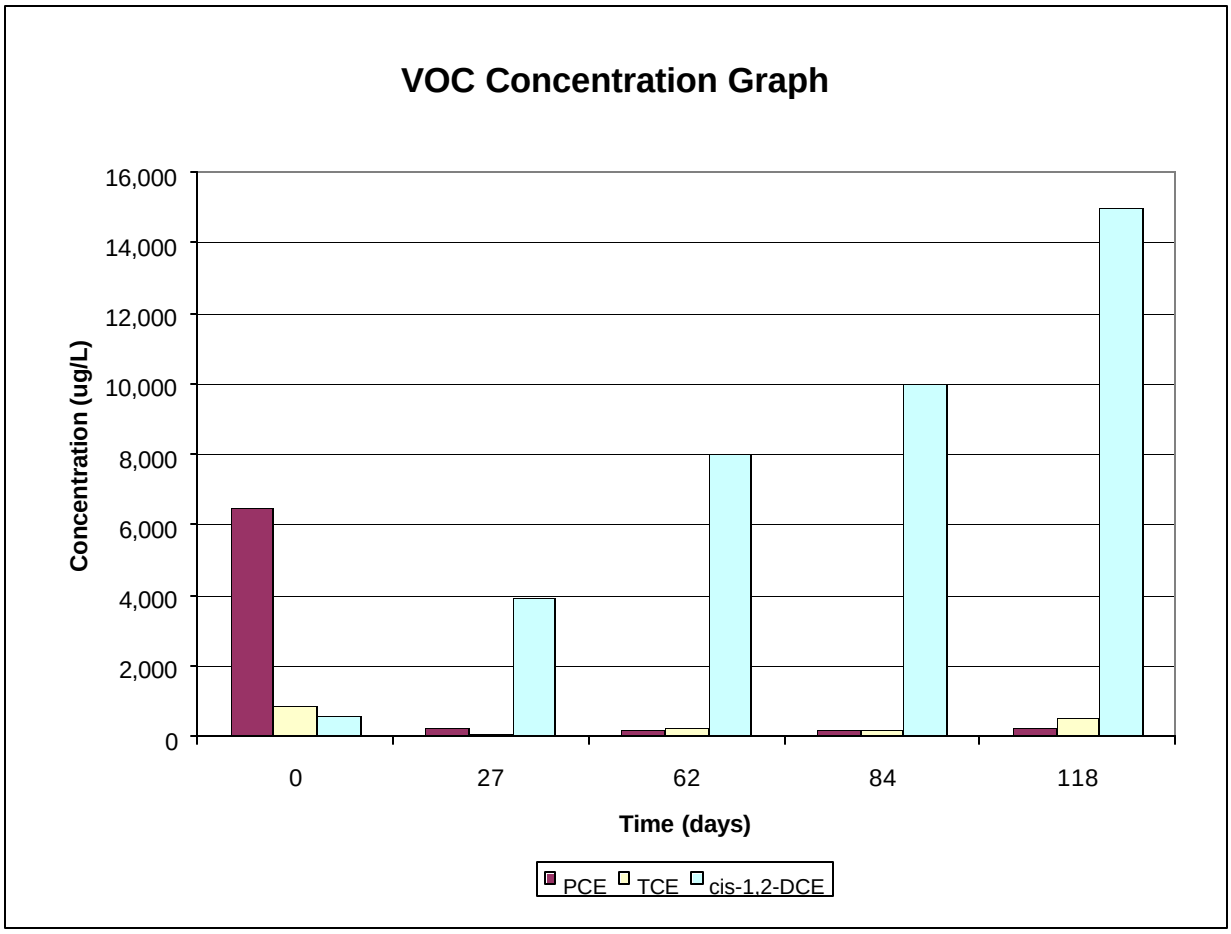

Figure 6. Harding Lawson Concentration Graph

Case 3: Project Conducted by ODEQ - Results from an Intentional DNAPL Remediation Effort

A site in Oregon was contaminated with PCE at concentrations reaching 120,000 ug/L in a silty sand aquifer. Groundwater velocity at this site is 0.3 ft/day, and depth to groundwater was recorded at approximately 5 ft bgs. Approximately 700 lbs. of HRC were injected into five points, covering a potential DNAPL area of 250 ft^2.

Figure 7 shows the results of the application through 286 days. PCE has dropped from 98,000 ug/L down to non-detect levels. TCE rose from 8,300 ug/L to 35,900 ug/L by day 197, and then dropped to 680 ug/L at day 286. DCE rose from 740 ug/L at baseline to 73,700 ug/L at day 286. Translating this into moles, a removal of 591 moles of PCE and 58 moles of TCE produced 753 moles of DCE, producing an exceptional mass balance. This indicates that the drop in PCE was a result of reductive dechlorination, and not a physical phenomenon such as a shift in direction or elevation of groundwater flow.

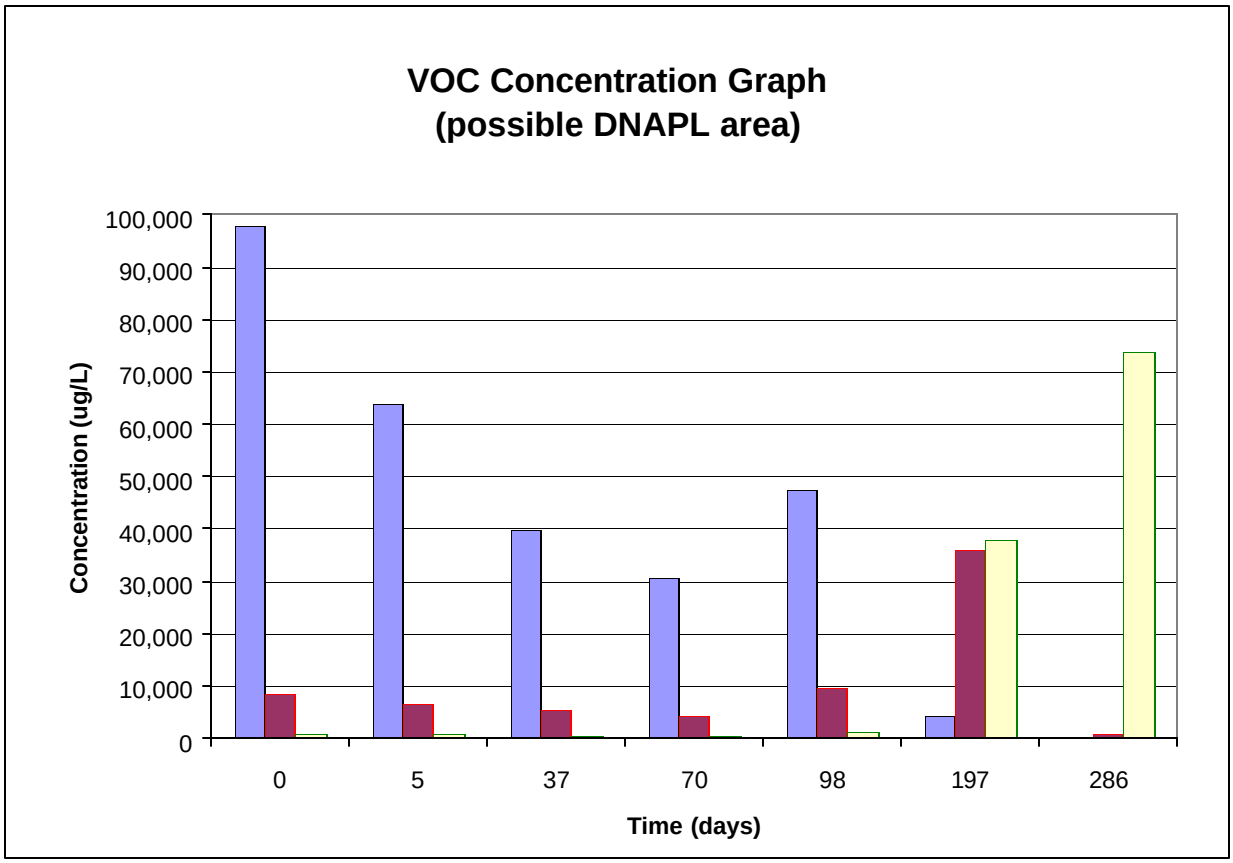

Figure 7. Oregon DEQ VOC Concentration Graph

Conclusion

Several lines of evidence point to the fact the HRC can stimulate the rapid desorption and degradation of hydrophobically sorbed and residual DNAPL. The literature is now beginning to actively report on this phenomenon and our own laboratory experiments verify these

observations. Some of our HRC treatment data sets are also able to reveal footprints of this facilitated desorption process as illustrated. In addition, one recent HRC treatment effort involved the intentional and hugely successful remediation of DNAPL. Clearly the use of HRC is a sensible strategy to treat appropriate levels of sorbed DNAPL, in addition to its classical application for treatment of dissolved phase plumes.

