

# Using HRC to Treat Residual Sorbed DNAPL Contamination

## General Background

While it is clear that bioremediation is effective against dissolved-phase contamination since it is readily available for microbial consumption, there has been debate about how readily sorbed contaminant can be treated. To facilitate discussion of this topic, some different types of DNAPL contamination are defined below.

## DNAPL Contamination

### Hydrophobic Sorption

This is generally a very low level of contamination that sorbs from a dissolved-phase plume to clean aquifer materials. Typically, clean soil will superficially adsorb a few multiples of the concentration of contaminant in the dissolved phase. If there is a significant amount of organic matter present in the soil matrix, there may be concentrations of contaminants as high as one to two orders of magnitude higher than the dissolved phase concentration, though this will still be a fairly low level when compared with the total mass of the system. In our standard HRC Applications Software, the hydrophobic sorption factor is a function of the  $K_{OC}$  (organic carbon). The software relies on published data sets for hydrophobic sorption under various conditions, with  $K_{OC}$  as a major contributing factor.

### Residual DNAPL

When pure solvent enters the aquifer, it sinks and as such, is classified as Dense Non-Aqueous Phase Liquid or DNAPL. The liquid will “finger” through the aquifer, forming “stringers” as well as droplets along its pathway. A small amount of residual mass will have a far greater impact on the aquifer than even a very high (100x) hydrophobic sorption value. These droplets which exist in macropores and stringers which connect through several pores are the main targets for HRC, beyond the dissolved phase and hydrophobically-sorbed contamination. The kind of contamination has also been shown to be effectively remediated through the active stimulation of reductive dechlorination.

### Free-Phase DNAPL

This is “free product,” a substantial amount of material that is usually only manageable through excavation, pumping, or some other intensive mechanical process. HRC is generally not recommended in these settings strictly from a stoichiometric perspective; there is just too much contaminant mass in free product for an affordable HRC application. However, in choosing a final technology, the decision must still be a function of the economic comparison to the next available solution for the problem, as well as a consideration of any special logistical constraints that would limit normal mechanical DNAPL removal operations.

In summary, HRC may be applied to address any site in which dissolved-phase and hydrophobically-sorbed contamination is of concern. The next challenge is to address the economical limits of HRC application in cases with residual DNAPL and, in rare instances, free-phase contamination.

## **Treating Hydrophobically-Sorbed and Residual Sorbed DNAPL**

### Why it Should Work

Microorganisms can accelerate sorbed contaminant removal through several mechanisms. Primarily, when microbes consume the “newly-born” dissolved phase that is outside an actively-desorbing source, they maintain a concentration gradient. As Fick’s Law states, the flux from the sorbed material will increase with the steepness of this gradient. Microbes may also actively secrete “biosurfactants” which facilitate desorption.

## **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).

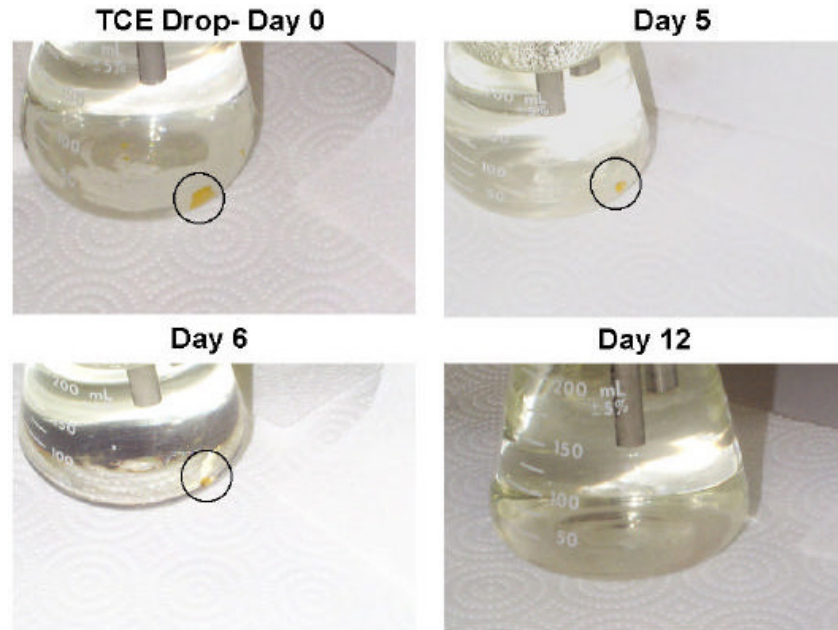
In the studies conducted, the effects of HRC upon chlorinated solvents in some or all the phases discussed above was investigated. Three types of experiments were performed:

### 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, it is clearly indicated that small globules of DNAPL can be completely removed relatively quickly from the aquifer solely through microbial consumption.



Figure 1. Experiment Set-Up

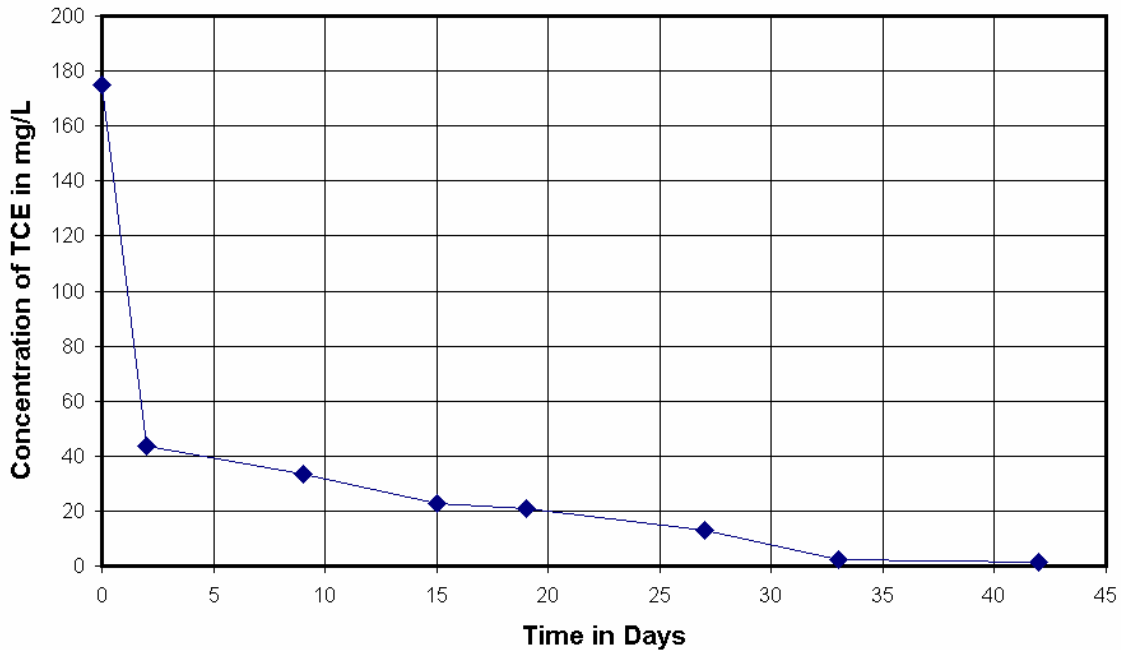


**Figure 2. Disappearing Drop Results from Baseline to Day 12**

### 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 display the action of HRC on the dissolved phase and the soil-bound hydrophobically-sorbed material that replenished the dissolved phase in accordance with Fick’s Law.

### Bioremediation of Pure TCE in Soil



**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. Each test tube contained 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, it 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 there was still a vary rapid removal of residual source due to microbial action.

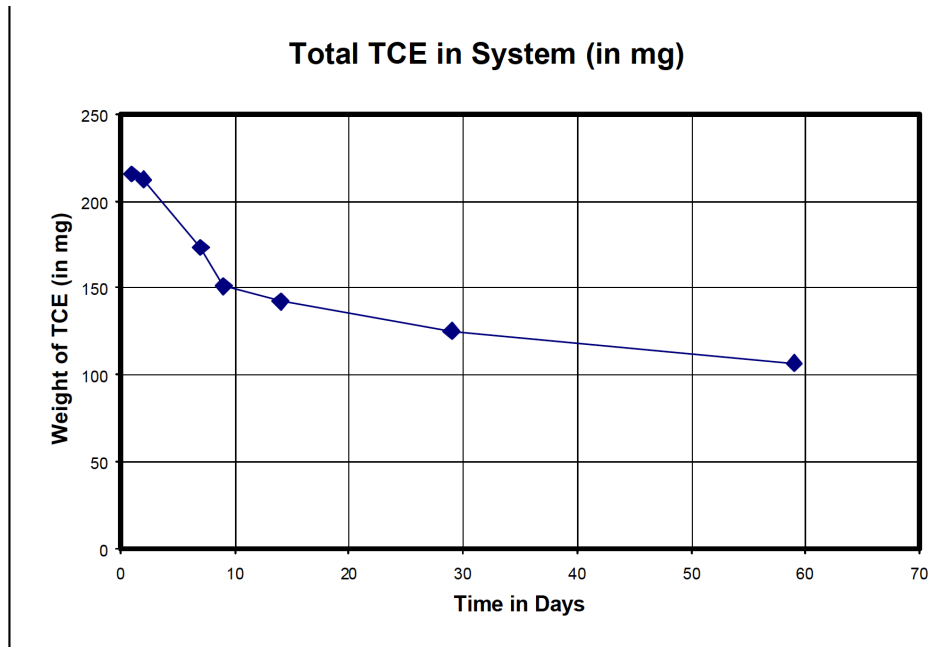


Figure 4. Results of the Modified Hughes Experiment

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 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 HRC-mediated bioremediation in some of our field work to date.

Considering a simple sequential dechlorination of TCE to its first daughter product DCE, some indirect evidence of desorption may be provided. Since TCE degrades more quickly than DCE, it may be hypothesized that an excess of DCE in the system over time would indicate the occurrence of desorption; as more TCE enters the system due to desorption, DCE levels will systematically increase. The DCE build-up is a function of the kinetic disparity, or the slower rate of removal of DCE relative to that of TCE.

This is observable in several site data sets, indicating the area treated contained some unknown residual. This is not uncommon—it is often hard to precisely locate a DNAPL source. In the data sets provided, a small reduction of TCE is accompanied by a larger increase in DCE, indicating the TCE pool is being “turned over” by desorption. Two examples are presented below.

#### 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 groundwater velocity (hydraulic conductivity = 0.01 ft/day). Depth to groundwater was recorded at approximately 5 ft bgs. Approximately 500 lb of HRC was injected into borings spaced 5 ft on center in a 560 ft<sup>2</sup> grid.

Figure 5 clearly shows that the DCE daughter product appears in excess of the TCE parent material over time. This data is particularly valid because it expresses total mass in the system as a function of a kreiging modeling exercise which can be used to 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 3.5x!

Between Day 89 and Day 166, a fairly robust reduction of both constituents is observable, but from Day 166 to Day 461, there is a clear buildup of DCE while TCE remains minimally changed. Also, from Day 166 to Day 273, there is a mass increase of 226g DCE with a loss of only 3g 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.

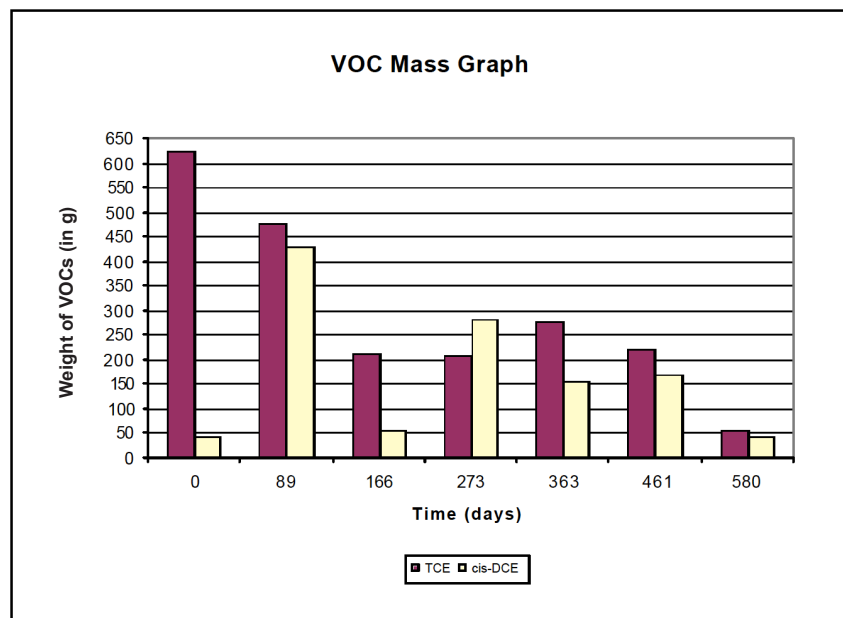


Figure 5. Haley & Aldrich Mass Graph

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 at 15 injection points.

Figure 6 displays the results from a single downgradient sentinel well. It clearly shows that the DCE daughter product appears in excess of the PCE parent contaminant over time. From Day 0 to Day 27, 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 desorbitive turnover of PCE and TCE.



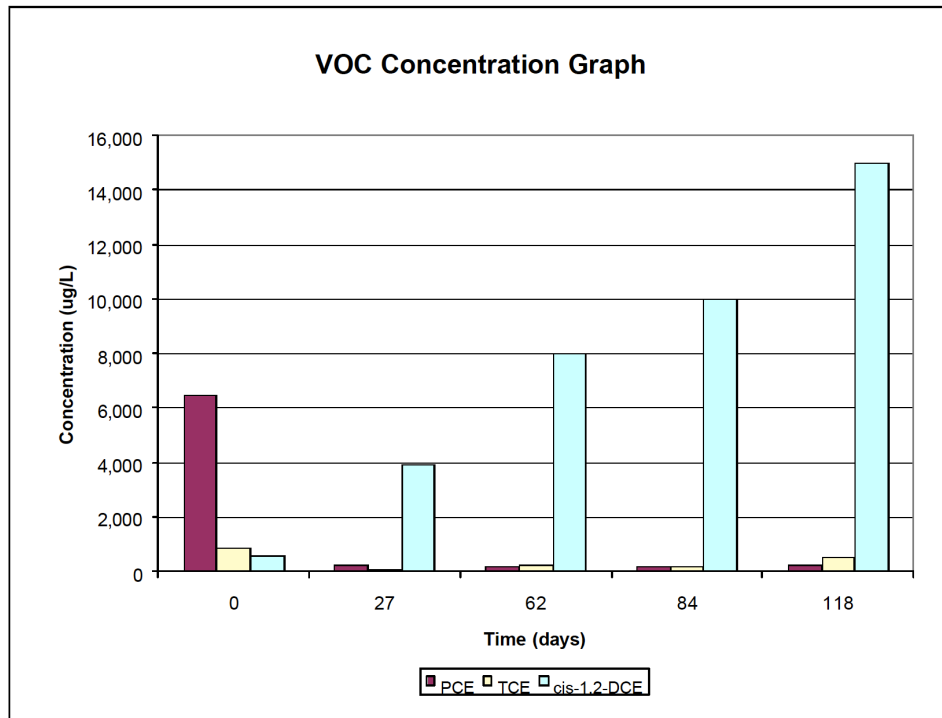


Figure 6. Harding Lawson Concentration Graph

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 lb. of HRC was injected into five points, covering a potential DNAPL area of 250 ft<sup>2</sup>.

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, not a physical phenomenon such as a shift in direction or elevation of groundwater flow.

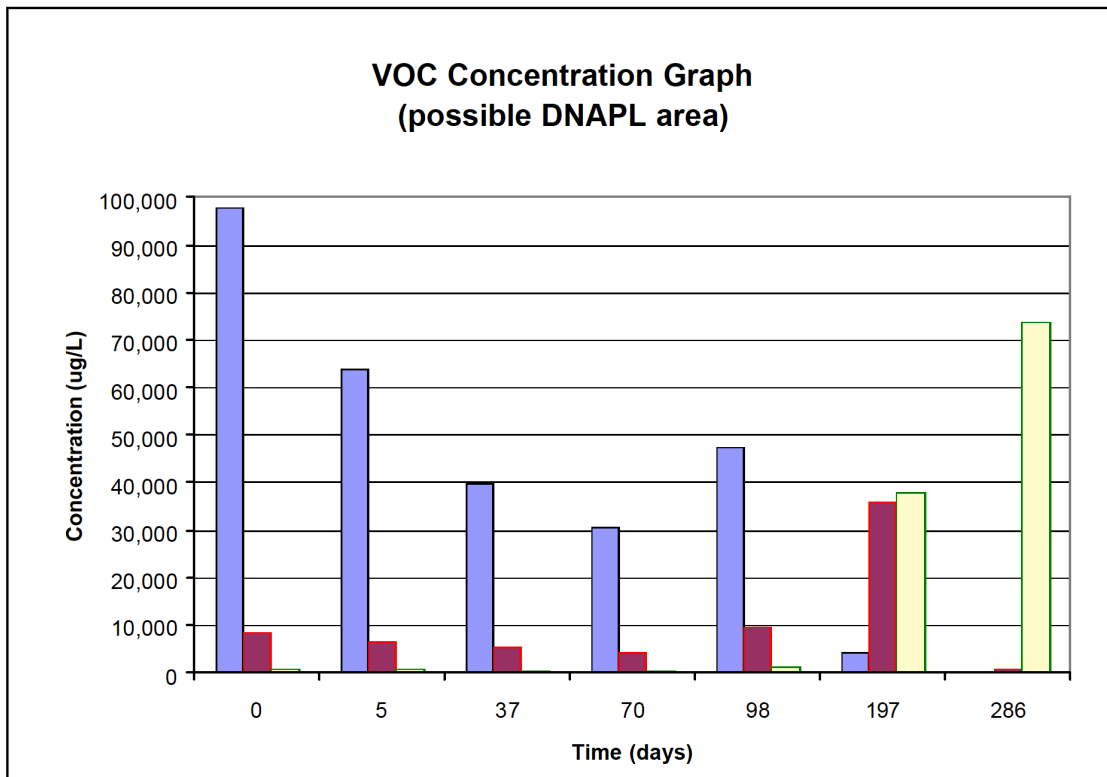


Figure 7. Oregon DEQ VOC Concentration Graph

## Conclusion

Several lines of evidence indicate that HRC can stimulate the rapid desorption and degradation of hydrophobically-sorbed and residual DNAPL. Available literature is beginning to actively report this phenomenon and our own laboratory experiments verify these observations. A few data sets from HRC applications are provided which depict this facilitated desorption process. In addition, one recent HRC treatment effort involved the intentional and hugely successful remediation of DNAPL. In addition to its previously-mentioned application to treat dissolved-phase plumes, HRC is a sensible strategy to treat reasonable levels of sorbed DNAPL.