CASE STUDIES IN ENHANCED REDUCTIVE DECHLORINATION

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ABSTRACT: Enhanced reductive dechlorination (ERD) is a groundwater remedial technology that entails injection of a mixture of highly biodegradable, soluble and colloidal organic carbon into a solvent-contaminated aquifer formation. The organic loading directs aquifer microbial consortia into low-redox behaviors such as sulfate reduction and methanogenesis. When sulfate-reducing or methanogenic conditions are established, chlorinated alkenes such as trichloroethene (TCE) and tetrachloroethene (PCE) can be reduced to ethenes and ethanes. Case histories are presented from two sites of chlorinated solvent contamination. At each site, carbon injections induced sulfate reduction and limited methanogenesis. At one site, a sandy aquifer formation was contaminated by PCE at 316 ug/L and TCE at 768 ug/L. During the first 6 months of carbon injection PCE and TCE concentrations declined, while cis-1,2-dichloroethene concentrations began to increase. Cis-1,2-DCE peaked at 2,700 ug/L after 9 months of injection, then was reduced 37 ug/L after 12 months. Less than 0.4 percent of the cis-1,2-DCE was converted to vinyl chloride (9 ug/L). The case history for the other site (fractured bedrock) shows comparable results.

EXTENDED ABSTRACT: Reductive dechlorination of chlorinated alkenes in aquifers can be enhanced through the injection of readily degradable carbonaceous materials such as molasses, whey or vegetable oil. Microbial degradation of the injected carbon consumes available electron acceptors such as oxygen and nitrates and forces the aquifer microbial communities into utilization of alternative electron acceptors such as ferric iron and sulfates. When sulfate-reducing or methanogenic conditions develop, chlorinated alkenes such as PCE, TCE, and cis-1,2-DCE can be rapidly dechlorinated. Reductive dechlorination reactions occur primarily in the aqueous phase. For many chlorinated alkenes such as PCE and TCE, a large portion of the mass in an aquifer can reside in the sorbed phase, unavailable to reductive dechlorination reactions. Aqueous-phase treatment processes such as enhanced reductive dechlorination generally require desorption of sorbed phase contaminants to achieve remedial objectives. Contaminants sorbed to "soft" forms of carbon such as poorly decomposed plant and animal tissues and non-target organic contaminants are more easily desorbed than those bound to "hard" carbon forms such as soot and charcoal that often occurs naturally in aquifer soils.

Figure 1 describes the portion of aquifer mass that resides in sorbed phase as a function of aquifer organic carbon fraction, for selected chlorinated alkenes. It was calculated from partitioning equations summarized in U.S. EPA (1996). At moderate levels of soil organic matter, less than 15 percent of PCE in an aquifer can be found in aqueous phase. Substantial mass transfer of contaminants from the sorbed phase to the aqueous phase must occur, along with reductive dechlorination reactions, to fully treat most aquifer formations. Four mechanisms associated with the enhanced reductive dechlorination process increase the availability of contaminants and are essential to the success of the technology. These four mechanisms include sequential partitioning coefficient (K_{oc}) reductions, dissolved organic carbon flooding, fermentation reactions, and biosurfactant production.
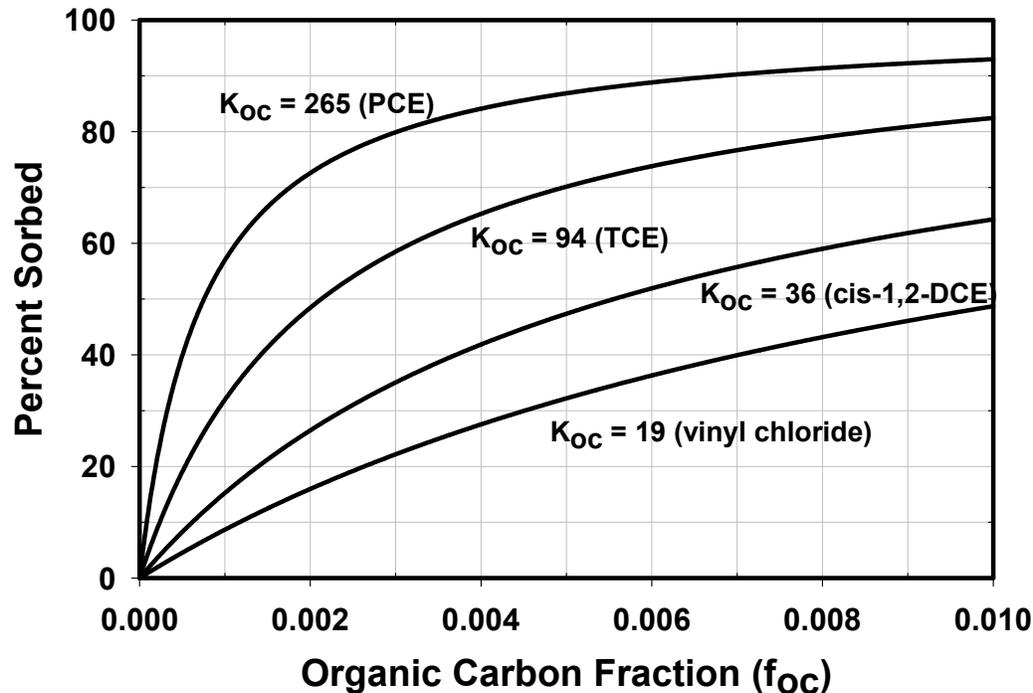
Figure 1. Percent of selected chlorinated alkenes predicted to reside in sorbed phase, as a function of the organic carbon fraction in the aquifer soil. In aquifer formations containing high organic carbon, only a small fraction of high-K_{oc} compounds such as PCE will be observed in aqueous phase. K_{oc} values were reported in U.S. EPA (1996) and are expressed as L/kg.

The two case studies discussed below demonstrate the net effects of interactions between enhanced reductive dechlorination and sorbed-phase chlorinated alkenes. The patterns observed are instructive because they clearly demonstrate rapid desorption and destruction of chlorinated alkenes.

High-Carbonate Porous Aquifer. A reactive zone was established in a porous, high-carbonate aquifer in the Midwestern U.S., that was contaminated by historic releases of PCE and TCE. The aqueous-phase PCE and TCE concentrations were 500 and 700 ug/L, respectively, prior to treatment. The sorbed-phase portions of these compounds that were not reflected in aqueous-phase measurements can be estimated from Figure 1. At a median organic carbon fraction of 0.003, 80 percent of the PCE and 58 percent of the TCE were expected to reside in sorbed phase prior to the start of carbon injections. Enhanced reductive dechlorination was induced through injections of 5 or 10 percent molasses solution every 2 weeks over a six-month period. Chlorinated alkene concentrations were observed at a groundwater monitoring well located approximately 30 meters downgradient from the reactive zone. As reductive dechlorination proceeded, a 6-fold increase in total dissolved alkenes was observed. This was consistent with the pattern shown in Figure 1, with the soil organic carbon fraction, f_{oc}, in the range of 0.006. The observed decrease in contaminant concentrations represented the combined effects of desorption and degradation. It is important to note that vinyl chloride did not accumulate during the study period. In addition, fermentation reactions were documented by the appearance of ketones at the carbon injection wells, but pH at the injection wells never fell below 5.5. At the downgradient monitoring well, the pH remained above 6.9 during all observations. This is a sharp contrast with the fractured bedrock study site,

where pH levels fell to 3.7 at the injection well. The dominant ketone at the study location was 2-butanone. Its concentration exceeded 13,000 ug/L in the injection wells and more than 3,000 ug/L were observed at the downgradient monitoring well. Ketones and other fermentation products are expected to degrade very rapidly downgradient from the reductive treatment zone.

Low-Carbonate Fractured Bedrock Aquifer. A reactive zone was established in a fractured, low-permeability bedrock formation in the Northeastern U.S., to treat an aquifer that was contaminated by PCE and trace amounts of its degradation products. The organic carbon fraction in this formation is approximately 0.001. A groundwater recovery system was operated in the source area for several years prior to implementation of enhanced reductive dechlorination, and a contaminant plume extended more than 500 meters from the source. Aqueous-phase PCE in the bedrock fractures was observed at concentrations up to 3,800 ug/L prior to starting the enhanced reductive dechlorination process. Molasses injections were conducted in the mid-plume area during pilot testing, then were expanded to allow treatment of the entire contaminated formation. A surge in the PCE concentration was observed in a source area monitoring well 60 days after injections were started in this area; the surge exceeded 94,000 ug/L. Carbon injections were stopped, but the PCE concentration continued to rise for a short period, peaking at more than 112,000 ug/L before returning to near-baseline levels. During this time, no significant degradation was observed. Source area molasses injections were restarted at a lower carbon feed rate on day 150 and the PCE concentration rebounded only to a fraction of its previous peak. Chlorinated alkene concentrations were also measured at a location approximately 30 days downgradient from the carbon injection location. The downgradient observations were consistent with the pattern expected to develop in the two stage process of enhanced reductive dechlorination. In the first stage, PCE concentrations remain stable initially, while reductive dechlorination products increase. Recruitment of PCE from sorbed phase sustains aqueous-phase concentrations during this stage, while the lower-K_{oc} degradation products accumulate in aqueous phase. In the second stage of the process, sorbed-phase PCE mass dwindles and its aqueous-phase concentration begins to decline. During this stage, degradation processes consume the TCE and cis-1,2-DCE. Ethene concentrations did not build up, although concentrations in a deeper well at the same location exceeded 500 ug/L. The cause of this distribution has not been determined. The enhanced reductive dechlorination process was slowed to control displacement of high-concentration groundwater observed in the pilot study area. Despite that restraint, significant reductions of chlorinated alkenes have been documented across the site.

Conclusions. Mobilization of sorbed-phase chlorinated alkenes (mass transfer from sorbed to aqueous phase) was clearly demonstrated in the case studies. The site with a well-buffered aquifer withstood heavy carbon loadings without an adverse pH excursion. The resulting releases of sorbed-phase alkenes, along with contaminant destruction under strongly reducing conditions, combined to generate net half-lives of 15 days or less and did so without the accumulation of vinyl chloride. In the poorly buffered fractured bedrock aquifer, there was a mobilization of sorbed-phase contaminant without their destruction, over a limited area. This required limitation of the carbon injection rate and led to a more restrained remedial program than was possible at the well-buffered, porous aquifer site. The fermentation-induced pH decreases may block development of the sulfate-reducing or methanogenic conditions critical to the reductive dechlorination processes. The well-buffered site showed no pH excursions, while the poorly-buffered aquifer fell to low pH only at the injection well.