

In Situ Chemical Treatment of Chlorobenzene and Chlorofluorocarbon DNAPL in Aquifer Materials under a Major River

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Background/Objectives. In situ chemical treatment is usually considered either oxidative or reductive. This dichotomy reduces applicability at sites impacted with a mixture of contaminants, some of which are susceptible only to oxidation and others to reduction. A residual DNAPL comprised predominantly of chlorobenzene, dichlorobenzene, and chlorofluorocarbons (CFCs), found in aquifer deposits under a major river offshore of an industrial facility, poses this problem. Chlorobenzene and dichlorobenzenes can be oxidized, while CFCs must be reduced. The DNAPL-impacted zone is found about 8 to 11 feet below the sediment-water interface. A conceptual remedy is to inject slightly soluble, solid potassium persulfate blended with a metal base, as a solid slurry into the impacted aquifer interval, via a barge-mounted direct-push system. The solids slowly dissolve over a long period of time, potentially decades, to release persulfate that is activated by the high pH base to generate hydroxyl radicals (strong oxidants to destroy chlorobenzenes) and superoxide radicals (reductant/nucleophile to destroy CFCs). Bench tests were designed to evaluate feasibility of this approach, either as a reactive treatment barrier (with single-pass columns) or treatment grid design (with recirculating columns).

Approach/Activities. DNAPL-impacted soil from the offshore treatment area was collected using a barge-mounted Vibracore. Groundwater was collected from an on-land monitoring well adjacent to the offshore area, from which a similar DNAPL has been recovered. Two types of column tests were conducted. Single-pass columns intended to simulate a treatment barrier consisted of a reagent layer comprised of potassium persulfate blended with calcium hydroxide placed between impacted soil layers. A total of 23 pore volumes of impacted groundwater was passed through the column. Composited effluent samples were collected after 5, 15, and 23 pore volumes, and soil was collected at the end of the test, for chemical analysis. For the second series, intended to simulate a gridded treatment area, 4 liters of impacted groundwater were continuously recirculated through the column at a rate equivalent to about 1 pore volume per day for 90 days. Water and soil were sampled at the end of the test. Samples were analyzed for VOCs, CFCs, RCRA metals, chloride and fluoride (as chlorinated VOC and CFC degradation products), and reagent components in both solid and aqueous phases.

Results/Lessons Learned. In the single-pass columns the concentration of chlorobenzene and dichlorobenzene in effluent was reduced by 99% and in soil by 90% relative to controls, with 98% chlorine mass balance (indicating little volatile loss). CFC degradation in the single-pass columns was mixed, with high variability and 122% fluorine mass balance, indicating either high soil sample heterogeneity and/or sorption from the dissolved phase. Final persulfate concentration was 23.5 g/L and pH was 12.3, indicating the reagent was not significantly depleted after 23 pore volumes. Recirculating column tests exhibited greater contaminant reduction and higher persulfate and pH persistence. Chlorobenzene and dichlorobenzene concentrations in the effluent and total mass were reduced by greater than 99.5% relative to controls. CFC concentrations were reduced by 40% in the effluent and 42% in total mass. Mass balance was 98% for chlorine and 96% for fluorine. Final persulfate concentration was 42 to 48 g/L and pH was 12.5 to 12.9, both higher than the single-pass columns. Key lessons learned are (1) both chlorobenzenes (degraded oxidatively) and CFCs (degraded reductively) are destroyed, and (2) increased residence time with higher pH and persulfate concentration in the recirculating columns improve CFC contaminant degradation.