Abiotic Reduction of Chloropicrin and Carbon Tetrachloride in Site Soil and Groundwater

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Background/Objectives. Groundwater at a confidential site in California is impacted with chloropicrin (500,000 mg/L) and carbon tetrachloride (2,200 mg/L). Chloropicrin is a broad-spectrum pesticide with a California notification level of 50 mg/L; carbon tetrachloride has a maximum contaminant level of 0.5 mg/L. In situ chemical reduction using zero-valent iron (ZVI) is being considered as a remediation option for the site. Although ZVI is an established technology for the dechlorination of carbon tetrachloride (CTET), limited data are available on the reaction with chloropicrin. Iron-sulfide minerals naturally present or generated via reduction of sulfate in the presence of ZVI can also potentially transform both chloropicrin and CTET. Bench-scale treatability testing was, therefore, conducted on site soil and groundwater to evaluate the ability of Z-Loy™ (a proprietary form of ZVI developed by OnMaterials) – with and without added electron donor – to destroy chloropicrin, CTET, and other chemicals of concern (COCs).

Approach/Activities. Batch tests using site soil and groundwater were conducted. Three series of reactors were prepared. One series contained soil and groundwater only and served as the controls. The second series contained soil, groundwater and 15 g/L Z-Loy™, and the third series contained soil, groundwater, 7.5 g/L Z-Loy™ and 7.5 g/L Newman Zone® (NZ, an electron donor). Dosing for Z-Loy™ and Newman Zone® were recommended by OnMaterials. Reactors containing Z-Loy™ were connected to Tedlar bags to prevent pressurization of the reactors. The reactors were shaken intermittently. At 2, 6, and 13 weeks, one reactor from each series was destructively sampled and the aqueous phases analyzed for chloropicrin, VOCs+TICs, anions (chloride, nitrate, nitrite, and sulfate), conductivity, DO, DOC (selected samples), ferrous iron, ORP, and pH. Measurable off-gases were generated for the Week 2 and Week 6 Z-Loy™ Only tests and were analyzed for chloropicrin and VOCs+TICs. Soil was not analyzed because COCs were not expected to strongly sorb to soil under the conditions of the test.

Results/Lessons Learned. Laboratory testing demonstrated that Z-Loy™, with and without added electron donor, could rapidly reduce concentrations of chloropicrin, CTET and other chlorinated VOCs. Complete dechlorination was confirmed in both the Z-Loy™ Only and Z-Loy™+NZ tests by the increase in chloride concentration. Methylamine, a potential by-product of chloropicrin reduction by ZVI, was not observed, possibly because methylamine is biodegradable. A small amount of methylene chloride, a common degradation product of CTET, was generated, but it accounted for less than 1% (mole basis) of the CTET initially present. Z-Loy™ and Z-Loy™+NZ decreased nitrate, DO, ORP and pH, and increased DOC and ferrous iron. All changes were indicative of the successful dechlorination of chloropicrin and CTET.