BIOREMEDIATION OF SOLVENTS IN FRACTURED ROCK GROUNDWATER RESULTING IN SIGNIFICANT VOC REDUCTIONS

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Abstract: Site investigations at a manufacturing facility in Virginia, USA delineated the presence of trichloroethylene; 1,1,1-trichloroethane; chlorinated breakdown products; acetone; and isopropanol in soil and groundwater in a fractured rock aquifer. In-situ cometabolic bioremediation through the injection of air, gaseous-phase nutrients (nitrogen and phosphorus), and carbon source (methane) was undertaken to stimulate existing microbial populations to promote and accelerate the degradation of target volatile organic compounds (VOCs). Monitoring data indicate that the enhanced bioremediation system has been successful in stimulating microbial growth based on increases in phospholipid fatty acid (PLFA) biomass and methanotroph measurements of several orders of magnitude within four months of system start-up. The initial total VOC concentrations ranged from 50,000 ug/l to >1,000,000 ug/l. Groundwater monitoring shows significant (90 to 99.96%) total VOC reductions in the pilot test area and in down-gradient monitoring locations since the initiation of the injection campaign. This confirms that the bioremediation process is very effective in treating VOCs in the source area, which leads to reduced VOC concentrations in down-gradient locations. VOC reductions of 99.99% have been observed in monitoring wells 75 ft down-gradient from the area affected by the injection system. As a result of the treatment system operation, groundwater in several monitoring locations now meets drinking water standards. Based on the pilot test observations, the system has been expanded to full-scale application to increase the delivery of the necessary amendments to target the entire area of concern. The expansion has resulted in further removal of VOCs in locations within the source area where previous results had shown limited improvement.

Numerous sites throughout the world have soil and groundwater contaminated with chlorinated hydrocarbons such as trichloroethylene, 1,1,1 trichloroethane, chlorinated daughter products and other solvents such as acetone and isopropanol. These diverse chemicals coupled with a complicated geologic environment such as clay and fractured bedrock create a challenging subsurface restoration project. Furthermore, the presence of complex systems of underground utilities limits the range of feasible remediation technologies at many sites. An in-situ soil and groundwater cometabolic bioremediation system was pilot tested by Earth Tech at the ITT Industries Night Vision manufacturing facility in Roanoke, VA. Based on the positive pilot test results, the bioremediation system was expanded to full scale and has been operating for one and one half years at full scale.

The selected bioremediation system was developed at the Westinghouse Savannah River Plant site (Hazen, 1995 and Hazen, 1996) and licensed by the U. S. Department of Energy. This system injects a gaseous phase mixture of oxygen (air), nutrients (nitrous oxide and triethyl phosphate) and carbon source (methane) to the targeted subsurface area to stimulate the growth of bacteria (primarily methanotrophs). These methanotrophic bacteria produce an enzyme (soluble methane monooxygenase) which degrades the chlorinated hydrocarbons (TCE, 1,1,1 TCA) and numerous other VOCs that include alcohols, ketones, and petroleum hydrocarbon constituents.

The chemicals of concern at the facility consist of the following: trichloroethylene (TCE), cis-1,2-dichloroethylene (cis-DCE) 1,1 dichloroethylene (1,1-DCE), vinyl chloride (VC), 1,1,1 trichloroethane (TCA), 1,1 dichloroethane (1,1-DCA), chloroethane (CA), acetone, and isopropanol. Although these VOCs have been detected at high concentrations, no discernible dense non-aqueous phase liquid (DNAPL) has been detected during the site investigations using a variety of methods. Based on the USEPA's "rule of thumb" where concentrations in excess of 1% of the solubility of the compound may be indicative of DNAPL, the presence of isolated DNAPL occurrences cannot be ruled out in discrete locations near the chlorinated hydrocarbon source area at this site. The subsurface geology consists of a silt and clay overburden underlain by an interlayered fractured shale and limestone. Groundwater is encountered in both zones between 5 and 15 ft. (1.5 to 4.6 m.) below ground surface (BGS) in this area.

The primary components of the bioremediation system consist of injection wells, monitoring wells, soil gas monitoring points, air compressor, gas cylinders, regulators, filters, flow meters, valves, and associated piping. The air, nitrous oxide, and triethyl phosphate are injected continuously while the methane is on a pulsed injection schedule of 8 hours per day, 5 days per week. The methane is injected at approximately 1% by volume, which is well below the lower explosive limit of 5 % for methane. The treatment system's effectiveness was monitored throughout the pilot phase and has continued during full-scale operation by low-flow groundwater sampling of the surrounding monitoring wells. Groundwater samples were collected following each of the three optimization phases (approximate two to three month interval) during the pilot phase. Less frequent (approximate 6 to 12-month interval) groundwater sampling has been implemented following the pilot phase. Groundwater samples were analyzed for VOCs, methanotroph most probable number (MPN) counts, phospholipid fatty acids (PLFA) total biomass, DNA testing for microbe identification, and general water quality parameters such as nutrients and metals.

Baseline (pre-start-up) microbial sampling results indicated that a diverse microbial community existed at the site. The target methanotrophic population was a minority of the total microbial community at the start of the injection process (average most probable number (MPN) 299). Following the addition of nutrients and carbon source, microbial data indicated that the methanotrophs had increased by one to four orders of magnitude (average MPN 1,226,459) and maintained these elevated levels during the full-scale operation of the treatment system. The total biomass based on PLFA measurements increased as well by one to three orders of magnitude from an average of 1.65 PLFA/ml filtered water to an average of 115 PLFA/ml filtered water. These significant increases in methanotrophs and biomass were observed once nutrients were injected. DNA results indicated increases in sMMO following nutrient and methane injection. The microbial data indicate the presence of the necessary bacteria and enzymes capable of degrading the site VOCs.

During the pilot test and subsequent full scale operation of the cometabolic bioremediation system, significant reductions in the target VOCs have been observed in all of monitoring wells located within the treatment area and two wells located down gradient. MW-306S, located at the former source (an underground waste solvent tank) contained the highest VOC concentrations on-site. MW-306S contained initial average isopropanol concentrations of 5,500,000 ug/l. The

isopropanol concentrations were recently reported at 350,000 ug/l which is a 94% reduction. TCE, cis-DCE, and VC concentrations in this well were initially detected at average concentrations of 68,000 ug/l, 64,333 ug/l, and 30,250 ug/l, respectively. Recent groundwater sampling results indicated that these compounds have been reduced as follows: TCE - 12 ug/l, cis-DCE - 100 ug/l, and VC – 10 ug/l. These reductions are on the order of 99.9 to 99.99% for the chlorinated hydrocarbon compounds.

Monitoring well MW-402 located immediately down-gradient from the source area and within the area affected by the injection system contained TCA, 1,1-DCA,, and chloroethane at average initial concentrations of 6,733 ug/l, 2,216 ug/l, and 179 ug/l, respectively. Recent groundwater sampling results indicated that the TCA, DCA and CA are currently at concentrations of 270 ug/l, 96 ug/l, and 33 ug/l, respectively.

Two monitoring wells that have shown the highest VOC reductions during the least amount of time have been MW-1 (shallow source area well) and MW-405 (located down gradient approximately 75 ft). Total VOC concentrations for MW-1 have been reduced from 196,360 ug/l to 20,000 ug/l during the first month of testing. The total VOC concentration is currently on the order of 100 ug/l with most of the compounds below USEPA maximum contaminant levels (MCLs). Total VOC concentrations for MW-405 have been reduced from an initial average concentration of 56,000 ug/l to 110 ug/l in approximately 5 months. Currently, the VOCs detected in this monitoring well are at or below USEPA Maximum Contaminant Levels (MCLs).

The results from the pilot testing and full scale operation of cometabolic bioremediation in a clay and fractured rock setting for solvents in groundwater indicate that this technology is a viable groundwater remediation technology that may be capable of approaching drinking water standards from initially very high VOC concentrations. This technology has also been applied at numerous other sites by a number of environmental consulting firms and organizations with favorable results for petroleum and chlorinated hydrocarbons.

References:

Hazen, T. C. 1995. Preliminary Technology Report for the In Situ Bioremediation Demonstration (Methane Biostimulation) of the Savannah River Integrated Demonstration Project, DOE/OTD [(u)]. U.S. Department of Energy Report, WSRC-TR-93-670, Westinghouse Savannah River Company, Aiken, South Carolina.

Hazen, T. C. 1996. Sanitary Landfill In Situ Bioremediation Optimization Test Final Report (U), WSRC-TR-96-0065, Westinghouse Savannah River Company, Aiken, South Carolina.