

Influence of Sulfate Reduction and Biogenic Reactive Minerals on Long-Term PRB Performance in a Sulfate Rich, High Flow Aquifer

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Background/Objectives. Historical grain storage facility fumigation operations resulted in groundwater carbon tetrachloride (CT) impacts in a small Kansas farming community. High site groundwater flow velocity (estimated at ~700 ft year) has resulted in the CT plume extending approximately 2,500 feet downgradient where it discharges into a small creek; the highest concentrations of CT (approximately 1,500 ug/L) are located near the source area. To limit further plume migration, a permeable reactive barrier (PRB) was installed across the plume width to passively treat CT. The PRB was constructed by injecting EHC[®] slurry in to a line of direct push injection points. EHC is composed of slow-release plant-derived organic carbon plus micro-scale zero valent iron (ZVI) particles. Inflowing groundwater is sulfate rich (~120 mg/L), potentially affecting substrate consumption rates and treatment zone reactive life. This presentation reviews geochemical parameter response and CT removal rates over time downgradient of the PRB and compares them with theoretical calculations on ZVI consumption rates using site specific data. These calculations are then discussed relative to the > 10 year PRB longevity and apparent mechanisms for the extended life.

Approach/Activities. 48,000 lbs of EHC was injected into an area measuring approximately 270 ft long x 10 ft wide x 9 ft thick on average. The PRB was installed along a road and extended across the width of the plume to limit further plume migration. PRB effectiveness is measured at two compliance wells located 70 and 140 ft downgradient from the PRB. Monitoring is performed on a bi-yearly basis and includes CVOCs and geochemical parameters. Total organic carbon (TOC) is monitored as an EHC reagent indicator while ORP, dissolved oxygen (DO), nitrate and sulfate are monitored to assess redox conditions in the downgradient zone. Direct measurements of iron have not been performed, but iron consumption rates have been estimated based on inflowing concentrations of terminal electron acceptors.

Results/Lessons Learned. CT removal rates peaked 16 months after installation at >99 percent removal. Two years after installation these rates decreased slightly to approximately 95 percent removal and have stabilized around that level for over ten years continuously supporting inflowing groundwater treatment. A significant increase in TOC was measured 70 ft downgradient from the PRB during the first two years. Since then, TOC levels have returned closer to background levels, suggesting that the more readily degradable carbon component (cellulose) had been consumed. During this initial phase redox conditions also reached their lowest point concurrently with significant reductions in inflowing nitrate and sulfate. After TOC levels returned closer to background, sulfate levels also moved closer to inflowing concentrations while ORP remained significantly below background. Theoretical ZVI consumption calculations suggest the ZVI may be consumed after 2.7 years if reacting stoichiometrically with inflowing sulfate. However, geochemical data suggest that ZVI by itself is not supporting significant sulfate reduction. The probable explanation for the long PRB reactive life is the formation of an iron sulfide mineral based reactive zone created downgradient of the PRB during the initial sulfate reduction phase and since acting as an electron reservoir. This zone may also be continuously rejuvenated by low levels of TOC in inflowing groundwater (~2 mg/L) and from the hydrogen produced from ongoing ZVI corrosion.