

Case Study of Monitored Natural Attenuation of Dissolved Chlorinated Hydrocarbons at a Former Railroad Maintenance Facility, Sanford, Florida

Locomotive and wheel maintenance activities resulted in the release of chlorinated solvents to soil and groundwater. An interim remedial action was performed, including the removal of 6,700 gallons of liquid and sludge from the maintenance pits, and the excavation of 6,000 tons of impacted soil. Twenty-five monitoring wells were sampled in the shallow water-bearing unit and analyzed for volatile organic compounds (VOCs). The primary chlorinated hydrocarbons detected were perchloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride (VC). Total chlorinated VOC concentrations ranged from <1 microgram per liter ($\mu\text{g/L}$) to 64 $\mu\text{g/L}$, and the maximum concentration of vinyl chloride (64 $\mu\text{g/L}$) indicated natural attenuation was occurring. A total of six wells in the upgradient, downgradient, lateral and source-area locations were also analyzed for natural attenuation parameters (general chemistry and hydrocarbon gases). The results indicate that PCE, TCE, cis-1,2-DCE and VC are naturally attenuating, and VC is degrading to ethane and ethene under reducing conditions. Anaerobic conditions for reductive dechlorination are evident in the affected area through denitrification, methanogenesis, sulfanogenesis, and ferric iron reduction. Natural attenuation is further being enhanced by relatively high alkalinity and a suitable pH range. Subsequent monitoring has been reduced to the six wells and monitoring results confirm that natural attenuation is continuing.

Historical locomotive and wheel maintenance activities using limited amounts of chlorinated solvents resulted in the release of contaminants to soil and groundwater. The source of contamination was determined to be in an area where locomotives were repaired, and spent solvents, water and sludges collected in concrete lined maintenance pits. The site is underlain by approximately 15 feet of fine-grained sand with small amounts of silt. A five-foot clayey sand aquitard separates the upper surficial water bearing zone from an intermediate water bearing zone. The depth to groundwater is approximately five feet. The shallow groundwater flows to the south.

In 1995, an interim remedial action was performed, including the removal of 6,700 gallons of liquid and 825 gallons of sludge from the maintenance pits, and the excavation of 6,000 tons of impacted soil. The concentrations of PCE in the soil ranged from <5.0 micrograms per kilogram ($\mu\text{g/Kg}$) to 1,000 $\mu\text{g/kg}$, concentrations of TCE ranged from <5.0 $\mu\text{g/Kg}$ to 60 $\mu\text{g/Kg}$, concentrations of cis-1,2-DCE ranged from <5.0 $\mu\text{g/Kg}$ to 5,400 $\mu\text{g/Kg}$, and VC was not detected in any soil sample.

In 1994, 15 monitoring wells were sampled to determine the shallow groundwater quality. The initial concentration of PCE ranged from <1.0 $\mu\text{g/L}$ to 160 $\mu\text{g/L}$, TCE ranged from <1.0 $\mu\text{g/L}$ to 23 $\mu\text{g/L}$, cis-1,2-DCE ranged from <1.0 $\mu\text{g/L}$ to 19 $\mu\text{g/L}$, and VC ranged from <1.0 $\mu\text{g/L}$ to 7.2 $\mu\text{g/L}$. Further assessment and monitoring of VOCs continued to evaluate shallow groundwater quality continued over the next several years. In general, the VOCs appeared to be naturally attenuating and compounds were only detected in a limited number of wells.

In December 1999, VOCs were only detected in groundwater samples from six of the 25 shallow monitoring wells when sampling for monitored natural attenuation parameters began. Detectable concentrations of PCE ranged from 2.1 $\mu\text{g/L}$ to 47 $\mu\text{g/L}$, TCE ranged from 1.2 $\mu\text{g/L}$ to 6.9 $\mu\text{g/L}$, cis-1,2-DCE ranged from 1.2 $\mu\text{g/L}$ to 8.3 $\mu\text{g/L}$, and VC ranged from 1.7 $\mu\text{g/L}$ to 64 $\mu\text{g/L}$.

A total of six wells in the upgradient (MW-29), downgradient (MW-32), lateral (MW-28) source-area (MW-25 and MW-27R) and flow path (MW-33) locations were also analyzed for natural attenuation parameters including permanent gases (oxygen, carbon dioxide, hydrogen chloride, and nitrogen), light hydrocarbon gases (methane, ethane and ethylene), and anion and cations (alkalinity, ferrous iron II, nitrate, nitrite, sulfate, sulfide, soluble organic carbon and iron). Field measurements of dissolved oxygen, redox potential, pH and temperature were also obtained. The wells were subsequently sampled in May and December 2000.

The results of the three sampling events indicate that PCE, TCE, cis-1,2-DCE and VC are naturally attenuating and VC is degrading to ethane and ethene under reducing conditions. Anaerobic conditions for reductive dechlorination are evident in the affected area through denitrification, methanogenesis, sulfanogenesis and ferric iron reduction. Natural attenuation is further being enhanced by relatively high natural alkalinity and a suitable natural pH range.

December 1999 Groundwater Quality Results

The process of reductive dechlorination requires an appropriate source of carbon for microbial growth to occur. Sufficient concentrations [>20 milligrams per liter (mg/L)] of anthropogenic carbon compounds have historically been detected in samples collected from MW-25R, MW-22R, MW-29, MW-32, and MW-33.

Field measurements of dissolved oxygen (DO) indicate that the area of affected groundwater was oxygen deficient at concentrations that allow reductive chlorination or oxidation of VC. The DO concentration in upgradient monitoring well MW-29 was measured at 1.4 mg/L. DO concentrations in samples from monitoring wells within (MW-25R) and downgradient (MW-32) of the area of the highest total dissolved degradation product concentrations were less than 1.1 mg/L. The DO concentration at lateral monitoring well MW-28 was 1.62 mg/L. The depletion of DO within the affected area indicated that aerobic degradation was occurring and that the anaerobic conditions needed for reductive dechlorination were present. There were corresponding elevated carbon dioxide (CO₂) concentrations within the area of affected groundwater. The CO₂ concentration at MW-25R (affected area) was 204.2 mg/L and the CO₂ concentration at MW-28 (lateral well) was 16.47 mg/L.

Sulfate was detected in samples from all monitoring wells in concentrations less than 20 mg/L and decreased along the flow path. Nitrate was detected in lateral well MW-28 at a concentration of 52 mg/L, but was not detected in MW-25R, MW-27, MW-29, MW-32, or MW-33. The depletion of sulfate and nitrate along the flow path, and in the area of highest total dissolved degradation products concentrations, is indicative of the microbially mediated processes of denitrification and sulfanogenesis occurring in the area of affected groundwater anaerobically degrading the chlorinated solvents.

Dissolved iron was detected in all samples collected at the site ranging from 0.3034 mg/L (MW-28) to 19.61 mg/L (MW-25R - affected well). Dissolved iron was detected at a concentration of 19.61 mg/L in the sample collected from MW-25R (the area of highest total dissolved degradation product concentrations). Samples from MW-27 (11.68 mg/L), MW-29 (14.04 mg/L), and MW-33 (13.0

mg/L) (potentially impacted wells) also had elevated iron concentrations in comparison to MW-28 (0.3034 mg/L) and MW-32 (1.219 mg/L), the lateral and downgradient wells, respectively. Elevated concentrations of ferrous iron II were detected in groundwater samples from MW-25R (8 mg/L), MW-27R (11 mg/L), MW-29 (13 mg/L), and MW-33 (13 mg/L). The samples from the lateral and downgradient wells, MW-28 and MW-33, respectively, were <1.0 mg/L. These data indicate that ferric iron is being reduced to ferrous iron as a result of the same anaerobic (electron rich) conditions that facilitate the reductive dechlorination of chlorinated solvents in the aquifer.

The alkalinity at the site is relatively high (66 mg/L to 160 mg/L) which is sufficient to buffer the potential changes of pH caused by biologically mediated oxidation reactions. The pH of the groundwater at the site ranges from 5.25 to 7.16. This range of pH is conducive to chlorinated hydrocarbon degrading microbes.

Methane was detected in MW-25R (the sample of the highest total dissolved degradation product concentrations) at a concentration of 4.173 mg/L and in the sample from upgradient well MW-29 (4.823 mg/L). In comparison, methane concentrations were 0.121 mg/L and 0.152 mg/L in groundwater samples from MW-28 and MW-32, the lateral and upgradient wells, respectively. Methane was also detected at MW-27R (1.801 mg/L) and MW-33 (1.995 mg/L), potentially impacted wells. Methane is produced under strongly anaerobic conditions, the same conditions that allow the reductive dechlorination of degradation products to occur.

Ethane and ethylene were detected in the sample collected from monitoring well MW-25R at concentrations of 6.719 $\mu\text{g/L}$ and 27.877 $\mu\text{g/L}$. These concentrations are elevated relative to the samples collected from MW-27R, MW-28, MW-29, MW-32 and MW-33 which did not exceed 0.5 $\mu\text{g/L}$. This indicates that VC (detected at 64 $\mu\text{g/L}$ in MW-25R), a daughter product of PCE and TCE, is naturally degrading.

Dissolved hydrogen concentrations ranged from 0.81 nanomolar (nM) to 3.38 nM. Concentrations ranging from 1 to 4 indicate sulfate reduction and concentrations greater than 1 nM indicate reductive dechlorination. If hydrogen concentrations are greater than 1 nM, rates of reductive dechlorination should have environmental significance and Type 1 and Type 2 behavior would be expected.

Summary

The changes in the properties of various halogenated compounds and the presence of anthropogenic carbon in groundwater strongly indicates that natural attenuation is occurring via a combined "Type 1 and Type 2 Behavior" as described in the USEPA's Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites. The recent groundwater sampling was designed to confirm whether there is a sufficient supply of electron donors, the role of competing electron acceptors and whether VC is oxidized or reduced. Subsequent monitoring has confirmed that natural attenuation is continuing.

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