

INTERACTION OF FUEL HYDROCARBONS AND CHLORINATED SOLVENTS AT AN AVIATION MAINTENANCE FACILITY

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ABSTRACT

Releases of fuel hydrocarbons and chlorinated solvents from a former waste management unit at an aviation maintenance facility have resulted in impacts to soil and groundwater. As a result of the fuel hydrocarbon releases, strongly reducing conditions have been created in the source area. This has resulted in reductive dechlorination through dehalorespiration. Outside the source area aerobic conditions exist, resulting in biologically mediated oxidation of fuel hydrocarbons and chlorinated solvent daughter products, including vinyl chloride. The overall rate of natural attenuation in groundwater is sufficient to prevent plume migration, allowing for site closure with no active remediation. In addition to examining the interaction of the fuel hydrocarbons with the chlorinated solvents, the impact of naturally occurring inorganic electron acceptors on plume behavior is discussed.

INTRODUCTION

The site is an active aviation maintenance facility for corporate aircraft. A 500-gallon underground storage tank was used as a waste management unit to store used aviation fuel, waste oil, and spent solvents starting in 1980. The waste management unit was decommissioned and removed in 1991. During the removal, evidence of a release was observed due to visibly stained soil. Confirmation samples collected from the excavation indicated the soil was impacted with fuel hydrocarbons and chlorinated solvents.

MATERIALS AND METHODS

In response to the discovered release, soil borings were performed to collect soil samples to determine the extent of the impact. Because the impacted soils extended into the saturated zone, an array of seven monitoring wells was installed and sampled. Groundwater is encountered at a depth of 12 feet in a silty sand unit, which is overlain by a clay confining unit. Hydraulic conductivity in the saturated zone is approximately 0.5 feet per day with an effective porosity of 35%. The typical gradient of 0.005 feet per foot yields a calculated groundwater seepage velocity of 0.007 ft/day.

Benzene, toluene, ethylbenzene and xylenes (BTEX) and chlorinated aliphatic hydrocarbons (CAHs) were identified as the chemicals of concern. Industrial solvents present in the dissolved phase plume include tetrachloroethene (PCE), trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA). In addition, CAH daughter products are present in the dissolved phase, including isomers of dichloroethene (DCE), 1,1-dichloroethane (1,1-DCA), vinyl chloride and chloroethane.

To better understand the groundwater conditions and the potential for natural attenuation as a dissolved-phase plume management strategy, a groundwater geochemistry monitoring program was initiated. Samples were analyzed for common inorganic parameters that can act as electron acceptors in biologically mediated reduction/oxidation reactions. Where measurements of electron acceptor concentrations were not reliable, concentrations of reduction by-products were measured instead (Weidemeir, et al, 1995a). For example, ferric iron (Fe^{3+}) is a potential electron acceptor, but it is insoluble. Therefore, ferrous iron (Fe^{2+}), the reduction by-product of ferric iron, was instead analyzed. In addition to the inorganic analyses, concentrations of ethene and ethane were measured, as these are products of complete dechlorination of CAHs. Groundwater samples were also analyzed for other indicators of natural attenuation. Table 1 shows the suite of groundwater analyses that were performed.

RESULTS

Analysis of the data which is representative of groundwater quality at the site indicates that:

1. Fuel hydrocarbons are not migrating from source area.
2. Highly oxidized CAHs are not migrating from the source area.
3. Products of partial dechlorination are migrating from the source area.
4. The partially dechlorinated CAHs are degrading rapidly once they leave the source area.
5. Methanogenesis is occurring in the source area.
6. Depletion of nitrate, ferric iron and sulfate occur both in the methanogenic source area and the area immediately adjacent to it.
7. High dissolved oxygen is present both upgradient and downgradient of the source area.
8. Reduction/oxidation potential (E_h) is significantly lower in the source area than in the upgradient and downgradient groundwater.

DISCUSSION

Through biologically-mediated redox reactions, dissolved phase fuel hydrocarbons have created strongly reducing conditions in the source area. The fuel hydrocarbons act as the electron donor, depleting dissolved oxygen, nitrate, ferric iron and sulfate, which act as electron acceptors (Weidemeir, et al, 1995b). As a result, methanogenic microbes can compete successfully in the source area, even though the rate of reaction for methanogenesis is significantly slower than reactions that utilize other common inorganic electron acceptors. Because of this differential preference, different zones have formed in groundwater at the site (Figure 1):

1. The anaerobic zone, where carbon dioxide is the primary electron acceptor, resulting in methanogenesis.
2. The anoxic zone, where sulfate, ferric iron and nitrate act as the primary electron acceptors. Dissolved oxygen is also present in this zone, but at low concentrations (<0.5 mg/L).
3. The aerobic zone, where oxygen is the primary electron acceptor.

The interaction of the fuel hydrocarbons, the CAHs and the inorganic electron acceptors at the site are fairly complex as illustrated in Figure 2.

The reduced conditions in the anaerobic zone are favorable for microbes that utilize CAHs as electron acceptors through dehalorespiration (Gosset and Zinder, 1996). As with inorganic electron acceptors, some CAHs are more favorable electron acceptors than others are. The more highly oxidized CAHs, such as PCE and 1,1,1-TCA are preferential to less oxidized species, such as vinyl chloride and chloroethane (Chapelle, 1996). This is because the rates of reaction for the more oxidized CAHs are faster than for the less oxidized CAHs. In the anaerobic source area, PCE and 1,1,1-TCA are degraded rapidly. This is evidenced by the lack of detections of these CAHs outside the anaerobic zone. Apparently, conditions are reduced enough in the anaerobic zone that even vinyl chloride is acting as an electron acceptor. This is indicated by the presence of ethene as a product of vinyl chloride dechlorination.

In the anoxic zone, degradation of the fuel hydrocarbons is completed, as evidenced by their absence in this zone. It is unclear how the less oxidized CAHs in the anoxic zone are reacting. Conditions are probably not reduced enough for vinyl chloride and chloroethane to act as electron acceptors in this zone. This is indicated by the lack of ethene detections in the anoxic zone. These less oxidized CAHs may be acting as electron acceptors in redox reactions where fuel hydrocarbons act as electron donors. Vinyl chloride may also act as electron donors in the anoxic zone. For example, microcosm studies have shown that vinyl chloride can act as an electron donor in a biologically mediated redox reaction where ferric iron is the electron acceptor (Bradley and Chapelle, 1996). 1,1-DCA and isomers of DCE may also act as electron donors under anoxic conditions through cometabolism. A possible primary substrate for this cometabolism is methane that has migrated out of the anaerobic zone. Chloroethane readily hydrolyzes abiotically under anoxic conditions (McCarty and Semprini, 1994).

In the aerobic zone, the remaining CAHs are degraded, evidenced by their absence in this zone. These less oxidized species, including DCE isomers, 1,1-DCA, vinyl chloride and chloroethane, appear to be acting as electron donors in this zone, with oxygen as the electron acceptor. 1,1-DCA, chloroethane and vinyl chloride can act as electron donors under aerobic conditions (Weidemeir et al, 1996). There is conflicting evidence as to whether or not DCE isomers can act as a carbon source under aerobic conditions (RTDF, 1996). However, aerobic cometabolism of DCE isomers is reasonably well established (Hirl and Irvine, 1997).

A spatial analysis was performed to determine natural attenuation rate constants through linear regressions (Buscheck, et al, 1993). Table 2 shows the results of this analysis. As indicated by the R^2 values, the validity of the analysis is good with the exception of PCE, 1,1-DCE and cis-1,2-DCE. The poor R^2 values for the DCE isomers is probably due to:

1. DCE being both created and destroyed through the dechlorination process.
2. DCE acting as both an electron acceptor and an electron donor within the plume.
3. Limitations of primary substrates for DCE degradation under cometabolism.

The poor R^2 value for PCE is due to destruction of PCE at a more rapid rate in MW-7, the area immediately beneath the source, which skews the curve fit. This is probably attributable to greater BTEX concentrations in the overlying source area soils. Apparently, fuel hydrocarbon electron donors are being contributed to the groundwater at a more rapid rate than in this area.

CONCLUSIONS

At this site, fuel hydrocarbons created anaerobic and anoxic conditions by depleting inorganic electron acceptors. In the absence of inorganic electron acceptors, other than carbon dioxide in the anaerobic zone, highly oxidized CAHs act as electron acceptors for fuel hydrocarbons. This dehalorespiration degradation results in partial dechlorination to less oxidized CAHs. The degradation of fuel hydrocarbons is completed in the anoxic zone, where oxidation of the partially dechlorinated hydrocarbons commences. The mineralization of the remaining CAHs is completed in the aerobic zone.

As a result of the interaction of the fuel hydrocarbons, the CAHs and the inorganic electron acceptors, the plume stabilizes at a short distance from the source. Because of this, natural attenuation is a feasible plume management strategy for this site.

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Table 1. Groundwater Analyses Performed

Analysis	Method
Volatiles Organic Compounds	EPA Method 8260
Methane, Ethane, and Ethene	RSKSOP-147
Sulfate	EPA Method 375.4
Nitrate	EPA Method 353.3
Dissolved Oxygen	Field Probe in Flow Through Cell/Hach Field Kit
Ferrous Iron	Hach Field Kit
Oxidation/Reduction Potential	Field Probe in Flow Through Cell
Temperature	Field Probe in Flow Through Cell
PH	Field Probe in Flow Through Cell
Conductivity	Field Probe in Flow Through Cell

Table 2. Degradation Rate Constants

Parameter	λ/v_x	R ² Value	Groundwater Velocity (ft/d)	Degradation Rate Constant (day ⁻¹)
<i>BTEX Compounds (Non-Chlorinated VOCs)</i>				
Benzene	0.0602	0.9427	0.007	4.30%
Toluene	0.0553	0.8038	0.007	3.95%
Ethylbenzene	0.0194	0.8038	0.007	1.39%
Xylenes	0.0429	0.8038	0.007	3.06%
<i>PCE-Based Compounds</i>				
Tetrachloroethene	0.0114	0.1662	0.007	0.81%
Trichloroethene	0.0379	0.8713	0.007	2.71%
cis-1,2-Dichloroethene	0.0580	0.6230	0.007	4.14%
1,1-Dichloroethene	0.0865	0.7331	0.007	6.18%
Vinyl Chloride	0.0785	0.8038	0.007	5.61%
<i>TCA-Based Compounds</i>				
1,1,1-Trichloroethane	0.0239	0.8958	0.007	1.71%
1,1-Dichloroethane	0.0147	0.7413	0.007	1.05%
1,2-Dichloroethane	0.0499	0.9564	0.007	3.56%
Chloroethane	0.0953	0.8038	0.007	6.81%
Vinyl Chloride	0.0785	0.8038	0.007	5.61%

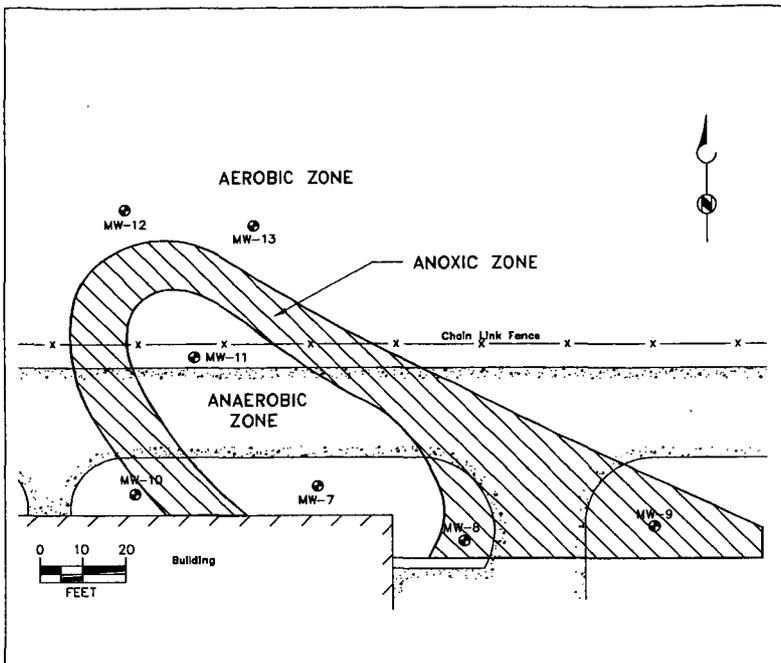


Figure 1: Groundwater Zones

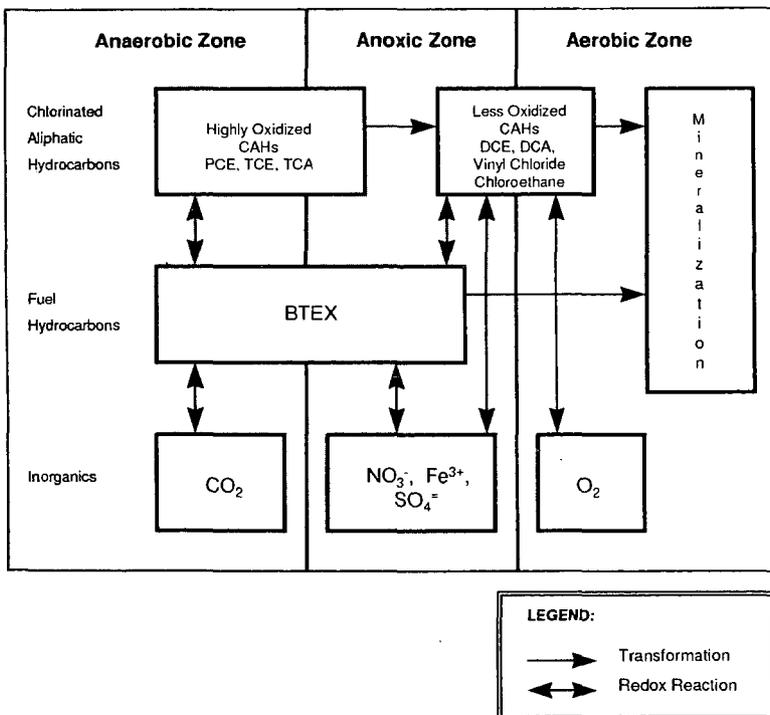


Figure 2: Chemical Interactions