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Soil Vapor and Groundwater Analysis from a Recent Oil Spill

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In northern Virginia, a fuel-storage terminal operated by a major oil company released approximately 200,000 gallons of liquid hydrocarbons into the underlying soil. The storage terminal is built on 5-10 feet of silty clay soil, which overlies 10-50 feet of chemically weathered rock, saprolite, which in turn overlies unweathered bedrock. The saprolite is the zone in which the water table and the overlying contamination plume are located at depths of 10-30 feet. The saprolite is composed of clay and various oxides, derived from the original mineralogy, plus as yet unweathered minerals most of which are quartz, feldspar, and mica. The mica imparts a planar fabric called foliation to the saprolite and to the underlying bedrock. The foliation is steeply inclined, almost vertical, and strikes to the northeast from the storage facility (Drake 1986). The groundwater is unconfined, and locally the water table can reach the surface during intervals of heavy precipitation (Prugh and Easton 1991).

The surface of the water table along the east side of the storage facility slopes down toward the east with a groundwater gradient of about 0.02 to 0.1 foot per foot (Prugh and Easton 1991). However, the hydrocarbon moves along narrow partings parallel to the northeasterly directed foliation surfaces (Obermeir and Langer 1986). The contamination plume migrated from the fuel-storage facility in a northeasterly direction in this narrow zone, approximately 200 feet wide, of enhanced permeability. By 1993, almost three years after the contamination was discovered, the plume reached almost 2,500 feet from its site of origin.

The origin of this narrow zone of enhanced permeability in the saprolite is probably related to weathering of the foliated saprolite under the storage-tank facility. Natural percolation of groundwater that entered the

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northeasterly partings in the foliation over geologic time has evidently formed pathways normally used by groundwater. The large volume of hydrocarbons passing through these pathways has contributed to increased solubility because of mixing.

In the following study, the soil vapor above the hydrocarbon plume and the groundwater below the product were analyzed for total petroleum hydrocarbons, TPH, and the individual hydrocarbons. The free product was also analyzed for the chemical identity of the fuel components present.

MATERIAL AND METHODS

The location of the fuel-storage site from which the hydrocarbon release occurred in northern Virginia is shown in Figure 1. The sampling site was directly over the thickest part of the hydrocarbon plume and is approximately 1000 feet northeast of the storage facility (ESE 1992). The water table under this area varied over a 3-5 foot interval depending on the season (Prugh and Easton 1991). At the time of sampling, the free product on the ground-water was several inches thick at a depth of 27 feet. Weekly measurements showed that free petroleum on the groundwater was as much as one foot thick.

Soil gas vapor analyses were accomplished by employing an AMS Soil Gas Vapor Probe. The probe was driven to a depth of 10 feet by a slide hammer. When the drive tubes are removed, the vapor probe tip remains imbedded at the desired depth. Fluorocarbon tubing, 0.22 inch i.d., running from the imbedded tip to the surface made continuous sampling possible. A Trace-Techtor, Hydrocarbon Vapor Tester (Lab Safety Supply Co.) was used to sample the soil gases. The meter was calibrated before each test with a standard, 440 ppm, hexane sample. The detector consisted of a hot filament coated with a platinum catalyst and protected by a sintered stainless steel sleeve to stop flame propagation in an explosive atmosphere. An identical detector filament that was not coated with the catalyst compensated for non-combustible gases. This meter does not detect methane.

The groundwater sample was placed in a 2-L separatory funnel, and the aqueous and petroleum fractions were separated. A 100-mL water sample was then adjusted to pH = 9 with Na_2CO_3. The water was subsequently extracted with two 50-mL portions of dichloromethane. The dichloromethane extract was reduced in volume at room temperature to 15-mL by rotary-flash evaporation. The concentrated extract was then dried over anhydrous magnesium sulfate.

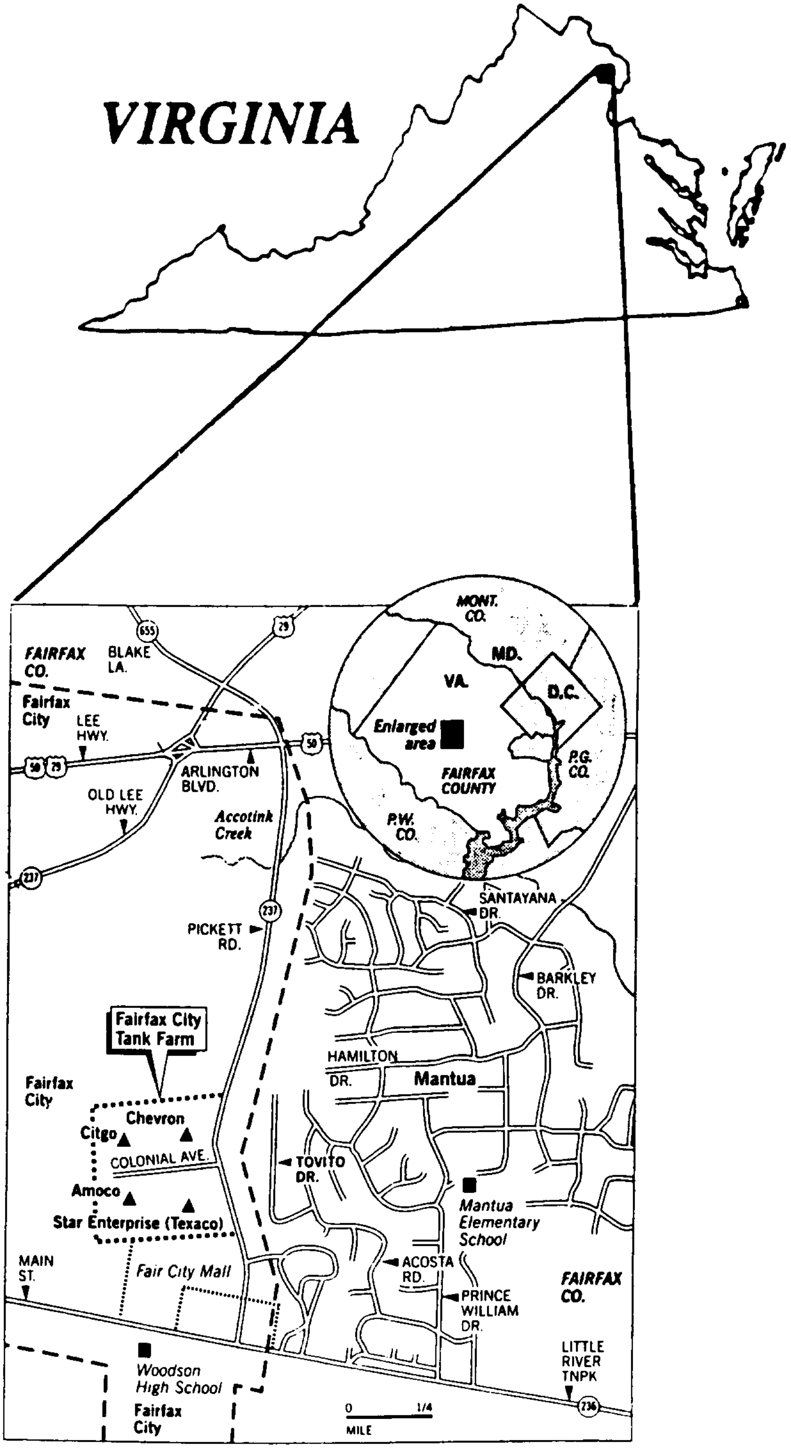

Figure 1. The oil spill site in northern Virginia

The petroleum compounds contained in the dichloromethane extract were identified by using combined capillary column gas chromatography/mass spectrometry. The GC/MS system consisted of a Finnigan INCOS 50B mass spectrometer equipped with a Hewlett-Packard 5890A gas chromatograph. The GC/MS was fitted with a 30 m x 0.25 mm DB-5 (95% dimethyl, 5% diphenyl siloxane; J & W Scientific) fused-silica capillary column that was operated with the following parameters: sample size - 2 μL, injector port - 250°C and configured for splitless injection, temperature program - 50°C/5 min, ramped at 4°C/min to 285°C with a 10 min final hold. These parameters gave the necessary resolution to distinctly separate and identify both the hydrocarbon and organonitrogen components. Internal standards were isopropyl benzene for the hydrocarbons and 2-(n-pentyl)pyridine for the nitrogen components.

The mass spectrometer was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from m/z of 50 to 550 daltons at a cycling rate of 1 scan/s. The mass spectrometer parameters were set up with the electron multiplier at 1050 V, source temperature of 200°C, and transfer line temperatures both at 290°C. The MS was tuned and calibrated with perfluorotributylamine immediately before use. The INCOS 50 data system software was used to process the acquired spectral information.

RESULTS AND DISCUSSION

With a spill estimated by the U.S. Environmental Protection Agency at approximately 200,000 gallons, the environmental implications for both the soil and groundwater are significant. The results reported here are from a monitor well that was about 1000 feet from the storage terminal. The water table at this well was approximately 27 feet when measured during the summer season.

Soil gases measured at a depth of 10 feet, Table 1, appear to be derived from the gasoline component of the subsurface plume supplemented by the low molecular weight compounds present in jet fuel. Because of their high boiling point, organonitrogen compounds were not observed in the soil gases. The soil effluent gases were collected in stainless steel gas collection bottles that had been evacuated prior to sampling. The sample bottles were subsequently connected to a manifold, heated to 100°C in an oven, and then sampled by the GC/MS. The compounds that were then identified were grouped and quantitated by area % as alkanes + alkenes, benzene, toluene, and ethyl benzene with a trace of xylene(s). Results showed alkanes + alkenes, ranging in size from C_4 to C_8, at a concentration of 6,600 ppm, benzene at 1,500 ppm, toluene at 1,160 ppm, and ethyl benzene at 760 ppm.

A value of 10,000 ppm TPH represents a level of contamination that has both health and safety concerns. If these gases were to collect in basements or sump spaces, the results show that they are well above explosive levels.

Table 1. Composition of Organic Vapor at a Depth of 10 feet.

Hydrocarbon Product	Concentration (ppm)
TPH (Gasoline)	10,000
Alkanes + Alkenes	6,600
Benzene	1,500
Toluene	1,160
Ethyl benzene	760

The petroleum liquid samples analyzed were from a monitoring well that had approximately 1 foot of hydrocarbon fuel, as free product, floating on the ground water. Migration of free product into a monitor well causes a depression of the water table, so the monitor well thickness of free product is about 10 times as thick as in the surrounding soil. Free product from the monitor well was analyzed by combined capillary column GC/MS (Keith 1992). The resulting chromatograms were analyzed first for petroleum product distribution; see Table 2. The hydrocarbon component distribution was assigned by taking the area percent of all compounds (1) from C_4 to toluene as representative of the gasoline fraction, (2) from toluene to C_{14} as representative of the jet A fraction, (3) from C_{14} to C_{20} representative of diesel fuel, and (4) above C_{20} representative of fuel oil. The GC/MS analysis of this free product revealed that jet fuel at 48% and diesel at 45% comprised the majority of the hydrocarbon material present, while gasoline and fuel oil were present at only 5 and 2%,

Table 2. Composition of the Free Hydrocarbon Product Above the Groundwater.

Hydrocarbon Components[a]	Concentration in Wt %
Jet A	48
Diesel	45
Gasoline	5
Fuel Oil	2

[a] Summation of peaks in the various boiling point ranges for the individual fuels

respectively. The quantity of each fuel was not as significant as the quantity of the individual components present. The low molecular weight components contribute not only to the ground water contamination, but more importantly to the soil gases that emanate from hydrocarbon liquids (Luckner and Schestakow 1991).

The ground water at this site is quite acidic, pH = 5.4. This is due to the absence of carbonate rocks as well as the extraction of polar acidic compounds, carboxylic acids, from the huge volume of petroleum products through which the water had to percolate to the water table. The dichloromethane extraction procedure has been shown to remove both hydrocarbons and basic nitrogen compounds such as the pyridines (Mushrush et al. 1986). Table 3 shows the GC/MS analysis for this groundwater extract.

Table 3. Composition of Dichloromethane Extract of Groundwater (pH = 5.4)

Contaminant	Concentration (ppm)
TPH	542
(B) Benzene	52.1
(T) Toluene	30.9
(E) Ethylbenzene	5.2
(X) Xylene(s)	2.8
Pyridine(s)	2.9

BTEX health and explosive dangers have been known for many years and have been widely reported in the literature. However, the dangers associated with nitrogen containing aromatic compounds have only recently been reported. Aqueous extracts of coal tars have been found to contain significant concentrations of pyridine compounds. The extracts were found to be very damaging to rat lung tissue (Perov 1972; Cohen 1985; Mead 1984). These studies proposed that the coal tar stimulated free radical reactions that caused cellular peroxidation resulting in lung tissue damage. The other organic components present in the aqueous extracts from coal tars were found to be non-damaging when the pyridine compounds were excluded (Pinsky and Bose 1988).

The slate of products in Table 3 shows that benzene, 52.1 ppm, and toluene, 30.9 ppm, predominated over the other hydrocarbons. Ethyl benzene, 5.2 ppm, and xylene(s), 2.8 ppm, represented the other aromatic hydrocarbons found. Trace quantities of alkanes along with alkyl substituted naphthalenes were found. Of the 2.9 ppm concentration of nitrogen heterocyclic compounds identified, they are mostly all monosubstituted alkyl pyridines. The alkyl substituted side chain was found to vary from C_3 to C_8.

Recovery efforts by the storage facility operators have lowered the water table in the sampling area by about 5 feet over the past 2 years. This means that another 5 feet of saprolite has been contaminated with hydrocarbons, thereby exacerbating rather than correcting the problem. Recovery efforts have diminished the free product on the water table, but no other remediation efforts have been attempted, even though soil vapor analysis points out both the health and explosive hazards.

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