A Comparison of Field Techniques for Confirming Dense Nonaqueous Phase Liquids

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Abstract

Dense nonaqueous phase liquids (DNAPLs) are immiscible fluids with a specific gravity greater than water. When present, DNAPLs present a serious and long-term source of continued ground water and soil contamination (Pankow and Cherry 1996). Accurate characterization and delineation of DNAPL in the subsurface is critical for evaluating restoration potential and for remedy design at a site. However, obtaining accurate and definitive direct evidence of DNAPL is difficult.

A field study was recently performed comparing several approaches to DNAPL characterization at a site where anecdotal and limited direct evidence of DNAPL exists. The techniques evaluated included a three-dimensional high-resolution seismic survey, field screening of soil cores with a flame ionization detector (FID)/organic vapor analyzer (OVA), hydrophobic (Sudan IV) dye-impregnated reactive FLUTe™ (Flexible Liner Underground Technologies) liner material in combination with Rotasonic drill cores, centrifuged soil with Sudan IV dye, ultraviolet light (UV) fluorescence, a Geoprobe® Membrane Interface Probe (MIP™), and phase equilibrium partitioning evaluations based on laboratory analysis of soil samples.

Sonic drilling provided reliable continuous cores from which minor soil structures could be evaluated and screened with an OVA. The screening provided reliable preliminary data for identifying likely DNAPL zones and for selecting samples for further analyses. The FLUTe liner material provided the primary direct evidence of the presence of DNAPL and reliable information on the thickness and nature of its occurrence (i.e., pooled or ganglia). The MIP system provided good information regarding the subsurface lithology and rapid identification and delineation of probable DNAPL areas. The three-dimensional seismic survey was of minimal benefit to this study, and the centrifuging of samples with Sudan IV dye and the use of UV fluorescence provided no benefit.

Results of phase equilibrium partitioning concentration calculations for soil samples (to infer the presence of DNAPL) were in good agreement with the site screening data. Additionally, screening data compared well with previous ground water data and supported using 1% of the pure phase solubility limit of Freon 113 (2 mg/L) as an initial means to define the DNAPL study area.

Based on the results of this study, the preferred approach for identifying and delineating DNAPL in the subsurface is to initially evaluate ground water data and define an area where dissolved concentrations of the target analyte(s) approach 1% of the pure phase solubility limit. Within this study area, the MIP device is used to more specifically identify areas and lithologic zones where DNAPL may have accumulated. Core samples (either Rotasonic or Geoprobe) are then collected from zones where MIP readings are indicative of the presence of DNAPL. Soil samples from the free-product portions of the core(s) are then submitted to a laboratory for positive analyte identification. Soil analyses are then combined with site-specific geotechnical information (i.e., fraction organic carbon, soil bulk density, and porosity) and equilibrium partitioning algorithms used to estimate concentrations of organic contaminants in soil samples that would be indicative of free product. Used in combination, the soil analysis and the MIP records appear to provide accurate DNAPL identification and delineation.

Introduction

DNAPLs are immiscible fluids with a specific gravity greater than water. Chlorinated solvents, creosote based wood-treating oils, and coal tar wastes are included in this group of compounds (Cohen and Mercer 1993). When present, DNAPLs introduce a serious and long-term source of ground water and soil contamination (Pankow and Cherry 1996). Additionally, the presence of DNAPL in the subsurface provides substantial site restoration challenges. The potential impact of DNAPL contamination on attainment of remediation goals is so significant that the United States Environmental Protection Agency (U.S. EPA) has developed specific recommendations for DNAPL site management (U.S. EPA 1993b). For instance, it may be technically impracticable to fully restore ground water or soil within DNAPL areas to precontamination levels in a reasonable time period using existing technology. Therefore, a goal of engineering or institutional controls may be established within the DNAPL portion of the site. Alternatively, considerable research is under way involving active remediation within DNAPL zones (visit http://gemin.getf.org/dnapl). In either case, accurately characterizing and delineating DNAPL is critical for evaluating the restoration potential of the site and for remedy design (U.S. EPA 1993b).

A study conducted by the U.S. EPA in 1993 concluded that up to 60% of National Priorities List sites may have DNAPL contamination in the subsurface (U.S. EPA 1993a). A large percentage of Resource Con-
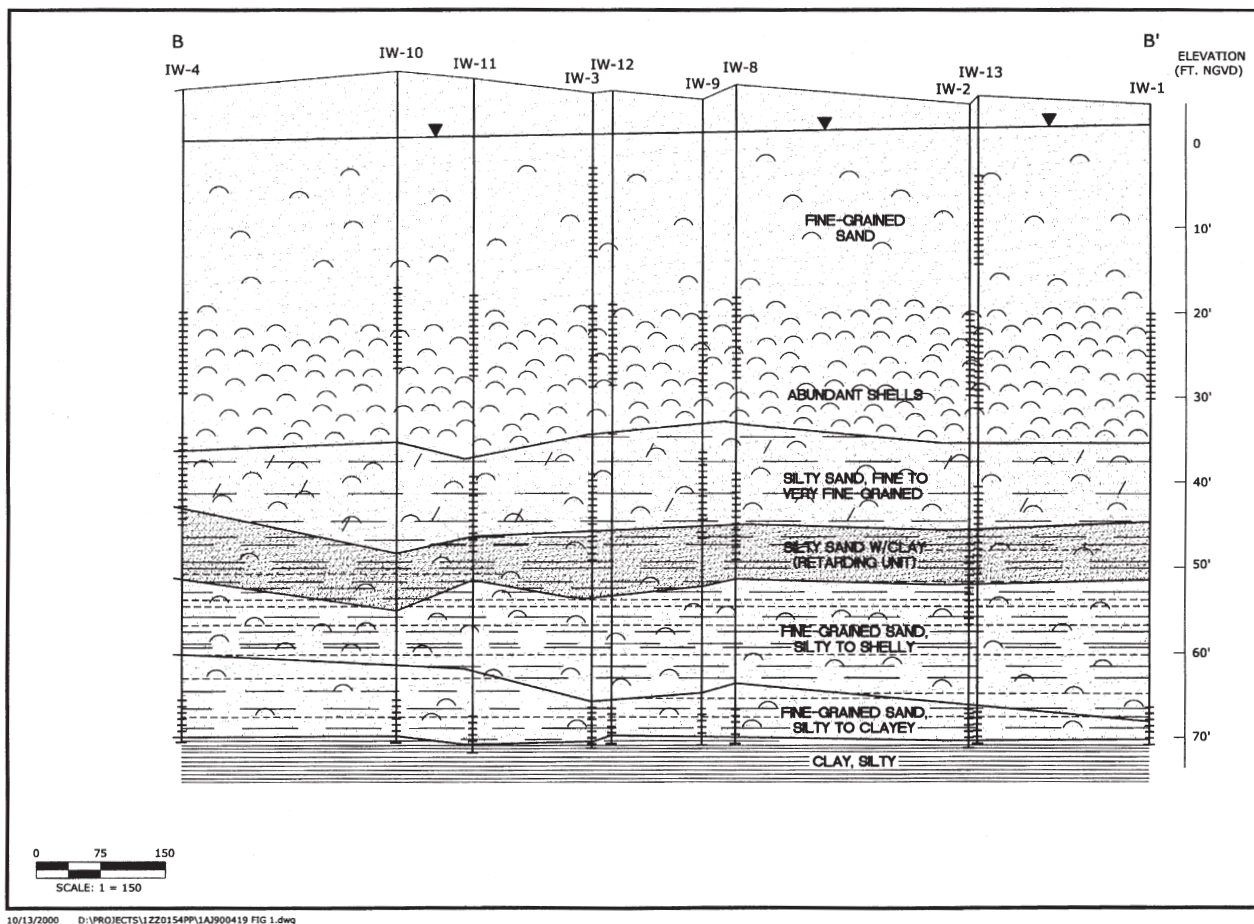
Figure 1. Geologic cross section B-B' Components Clean Facility.

servation and Recovery Act (RCRA) corrective action facilities also contain DNAPL contamination. While it is generally agreed that DNAPL is present at many industrial sites, this conclusion is frequently based on circumstantial evidence alone. This is due to the difficulty of obtaining direct evidence of DNAPL in the field. Examples of circumstantial evidence of DNAPL include dissolved contamination at concentrations greater than 1% to 10% of the pure phase chemical solubility— a concentration distribution wherein significantly higher contaminant concentrations exist at depth—and chemicals in soils exceeding 1% of the estimated soil mass (Cohen and Mercer 1993). To develop a sound strategy for DNAPL remediation, a more accurate means of DNAPL detection and delineation is desirable.

The objective of this study was to evaluate several of the more promising and innovative approaches to DNAPL characterization in the field at a location where indirect and limited direct evidence of DNAPL exists. The techniques evaluated included field screening of soil cores with a flame ionization detector (FID)/organic vapor analyzer (OVA), hydrophobic (Sudan IV) dye-impregnated reactive FLUTe liner in combination with Rotasonic drill cores, centrifuged soil with Sudan IV dye, ultraviolet (UV) light fluorescence, Geoprobe's Membrane Interface Probe, and direct soil analysis. A three-dimensional high-resolution seismic survey of the site was also conducted to locate potential DNAPL

migration pathways and trapping structures for DNAPL accumulation. This information was used to optimize soil core sample locations.

Site Conditions

The Components Clean Facility (CCF) site at the National Aeronautics and Space Administration's Kennedy Space Center near Titusville, Florida, was selected for this study. The CCF site encompasses nearly 17 acres and has been used since the early 1960s for cleaning and refurbishing predominantly stainless-steel hardware in support of space exploration operations. Cleaning operations typically included precleaning of parts in ultrasonic vats and vats of cleaning agents (predominantly chlorinated solvents). The most prevalent solvents used at this facility have been 1,1,2 trichloro-1,2,2 trifluoroethane (Freon 113), other freon products, and trichloroethene (TCE). Current management of waste solvents greatly minimizes the potential for releases; however, it appears that surface discharges and discharges from underground sumps may have occurred in the past.

An RCRA facility investigation began at the CCF site in 1994. This investigation confirmed the presence of high concentrations of Freon 113 and TCE in the subsurface, including at least one direct-push technology ground water sample in which phase separation of water and a dense immiscible fluid was observed in the sample vial.
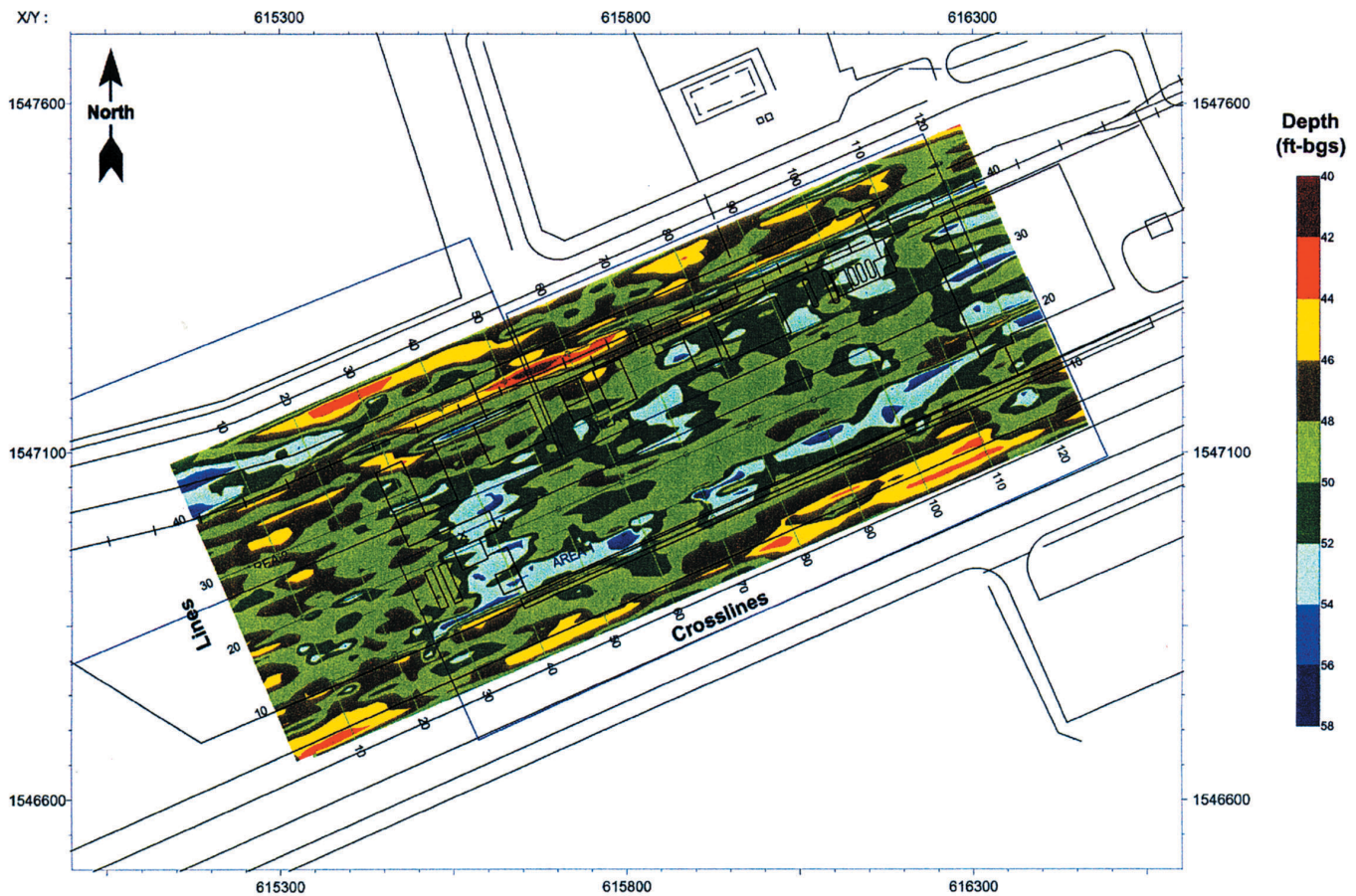
Figure 2. Seismic cross section line 30 Components Clean Facility.

The CCF site hydrogeology has been investigated to a depth of approximately 100 feet below land surface (bls). A geologic cross section for the CCF site is presented in Figure 1. The upper 20 to 25 feet of the subsurface consists of light to dark brown, fine-grained sand. Deposits about 20 to 35 feet bls consist of greenish-gray, fine-grained sand with increasing amounts of medium to coarse shell fragments with depth. The base of this unit is composed almost completely of shell material and produces considerable quantities of water. From about 35 to 45 feet bls, the shell content decreases and the sand becomes fine-grained to very fine-grained and silty. This lithologic change likely represents the transition from largely undifferentiated Holocene and Pleistocene deposits to Pliocene deposits. Silty fine-grained to very fine-grained sands occur from about 45 to 55 feet bls. The quantity of shells is reduced in this unit and the sand becomes interlayered with thin clayey silts, ranging from 2 to 10 inches thick. This unit is considered a hydraulic retarding unit because the overlying and underlying strata are more permeable. Fine-grained sand containing varying amounts of silt, clay, and shell occur from the base of the retarding unit to roughly 70 feet bls. At this depth, lower permeability silty clays and clayey silts are present. These silts and clays are interpreted as the top of the

Miocene Hawthorn Group. Shelby-tube samples collected from the upper portion of this unit were classified as sandy to clayey silts with an average permeability of 0.002 foot/day.

Investigation Methods

Three-Dimensional High-Resolution Seismic Survey

Three-dimensional high-resolution seismic surveys have been applied to DNAPL site characterization efforts (Adams et al. 1998; Geller and Myer 1994). Reportedly, organic liquid compounds in the subsurface can attenuate a seismic signal, and this attenuation can potentially provide a diagnostic tool for identifying DNAPL ganglia in the subsurface. However, other studies have indicated that this is unlikely due to rapid travel times associated with shallow seismic images and their inability to produce accurate readings on the scale required to identify phase variability of liquids in the subsurface (Lifsher 1999).

A three-dimensional high-resolution seismic survey was performed as the initial phase of this investigation. The primary objectives of the survey were to create a three-dimensional image of the subsurface structure and stratigraphy beneath the study area, from the near surface

Figure 3. Depth map of the retarding unit surface three-dimensional high-resolution seismic survey interpretation (50 ± feet bls).

to a depth of more than 100 feet bls, to delineate potential trapping structures for DNAPL ganglia and pools, and to delineate potential shallow migration pathways from the likely DNAPL (release) sources to the trapping structures. A secondary objective of the survey was to evaluate seismic data within a confirmed DNAPL area to determine if signal attenuation was evident. The survey was conducted by Resolution Resources Inc. of Minneapolis, Minnesota, using a 20-foot grid spacing over an area of roughly 480 by 1200 feet. The seismic reflection survey was performed using a 144-channel seismograph system triggered by a seismic source (elastic wave generator or hammer). Three 48-channel seismographs were used to record the data. The data were converted to Society for Exploration Geophysicists Format Y (SEG Y) and were stacked with the traces arranged in a three-dimensional matrix of traces. An example seismic cross section and structure map near the 50-foot-deep retarding unit is provided in Figures 2 and 3, respectively. The upper (red) line in the cross section represents (roughly) the top of the 50-foot-deep retarding unit. The lower black line surface represents the top of the Hawthorn Group clays at approximately 70 feet bls. Where possible, core locations were located to test structural lows associated with nearby fracture planes/fault traces.

Sonic Coring and Reactive Strip Evaluation

Rotasonic or sonic drilling techniques were used to obtain continuous cores at all sample locations (except the subsequent MIP locations). Sonic drilling refers to a dual-cased drilling system that uses high-frequency mechanical vibration to take continuous core samples of both unconsolidated and consolidated formations. Sonic drilling was used because continuous 4-inch-diameter cores could be collected wherein small-scale soil structure could be observed. This technique also minimized or eliminated the chance of sample or formation cross-contamination by use of a dual-casing system and minimized the amount of investigation-derived waste generated. Additionally, the reactive strip material could easily be inserted within the flexible plastic core sleeves.

For each core interval of interest, a 3-inch-wide strip of reactive flexible liner material was placed within the plastic core bags prior to core extrusion. The flexible liner material was constructed of hydrophobic Tyvek™ material and was impregnated with similarly hydrophobic (Sudan IV) dye. The flexible liner is designed to turn bright red in areas where hydrophobic, immiscible organic solvents come into contact with the impregnated material. The material was provided by Flexible Liner Underground Technologies Ltd. Co. of Santa Fe, New Mexico. The procedure used in this study was a modification of the typical procedure wherein the liner is placed wholly within an open borehole as the drill casing is removed (Riha et al. 2000). After sufficient contact time, the reactive liner is retrieved using a tether device. During this investigation, one core was extruded directly into a complete FLUTe liner core bag; however, staining was not
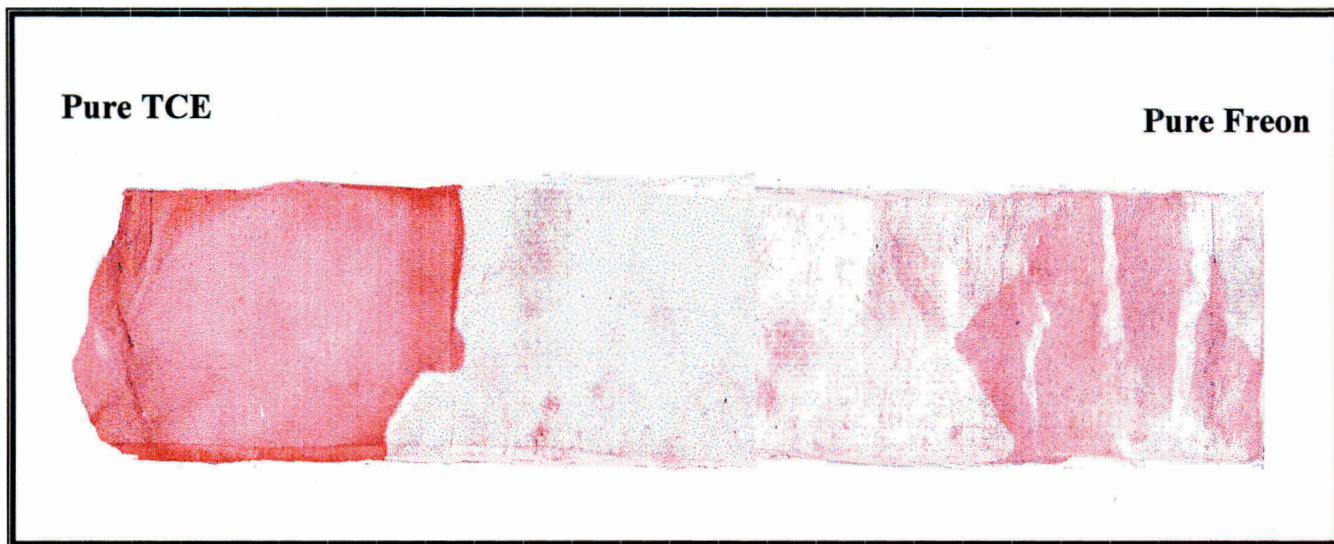
Figure 4. FLUTe liner reactions to chlorinated solvents.

noted within that core interval. A test strip of the material clearly shows the presence of both Freon 113 and TCE (Figure 4). However, the Freon 113 staining of the material is much fainter than for TCE.

OVA Screening of Soil Cores

Soil samples were collected from select portions of the initial cores and head space analyses of organic vapors were performed using a method prescribed by the Florida Department of Environmental Protection (Florida Administrative Code [FAC] 62-770.200[2]). A Heath Tek PortaFid II (FID) was used for the soil vapor screening, with and without the use of a charcoal filter, and net values were reported. Direct readings also were taken within the core bags by cutting a roughly 3-inch-long slice in the core bag, opening a void space within the core, inserting the FID tip within the void space, and sealing off the open slit with cupped hands. The results of the later technique can be performed more quickly than the headspace method and the vapor readings from both were nearly identical. This allowed for rapid screening of subsequent cores at roughly 2-foot intervals.

Hydrophobic Dye Shake Test and Centrifugation

Based on the OVA readings and observations of FLUTe liner reactions, aliquots of soil were collected from select portions of the cores for additional analyses using a hydrophobic dye shake test and centrifugation method described by Cohen and Mercer (1993). Specifically, approximately 20 cm^3 of soil were transferred to a 50 mL polypropylene centrifuge tube, approximately 20 mL of dionized water was added, and the sample was centrifuged at approximately 1250 revolutions per minute (rpm) for roughly one minute and evaluated to see if liquid phase separation was apparent. Roughly 2 mg of powdered hydrophobic Sudan IV dye were then added to the tube and the sample shaken vigorously to ensure adequate contact of the dye throughout the sample. The tube was again centrifuged for roughly one minute to facilitate

phase separation. Any DNAPL separation (i.e., red liquid at the bottom of the centrifuge tube) was then noted.

UV Fluorescence Analysis

Fluorescence refers to the spontaneous emission of visible light resulting from a concomitant movement of electrons to higher and lower energy states when excited by UV radiation (Cohen and Mercer 1993). While many organic contaminants fluoresce to varying degrees (e.g., aromatic or polyaromatic hydrocarbons and PCBs), saturated aliphatic hydrocarbons generally do not fluoresce unless mixed with fluorescent impurities. While significant direct fluorescence of the contaminants of concern was not anticipated, UV fluorescence of associated inorganic impurities was considered possible, and this technique was evaluated as a potential useful DNAPL characterization method.

Membrane Interface Probe (MIP)

The MIP is a direct push technology-based sampling method developed by Geoprobe Systems (Christy 1996). MIP services were provided by Zebra Environmental Corp. The MIP system consists of a thin film fluorocarbon polymer membrane mounted on a stainless-steel drive point. The drive point is advanced using direct-push (Geoprobe) technology. The membrane is heated to approximately 100°C to 120°C and a clean carrier gas (nitrogen, helium, or purified air) is circulated across the internal surface of the membrane. Volatile organic compounds (VOCs) that partition across the membrane are subsequently measured by a conventional detector system (e.g., gas chromatograph [GC]/mass spectrometer [MS], photoionization detectors [PIDs], flame ionization detectors [FIDs], electron capture devices [ECDs]) at the ground surface. A continuous log of VOC detections versus depth is generated. Soil conductivity and penetration rate information are also provided by use of a conductivity dipole and other sensors, providing real-time lithology-based data for interpretation.

Table 1
Comparison of Representative DNAPL Field Test Results
CCF DNAPL Investigation
February–March, 2000

Depth (ft bls)	Visual Observation	Ultraviolet Lamp	Sudan IV Shake	Post Centrifuge Observation	Organic Vapor Concentration (ppm)	FLUTe Liner Indication	Analytical Result (mg/kg)
Soil Boring SB-5							
38	ND	ND	ND	ND	3800	None	Freon – **304**
Soil Boring SB-6							
23	ND	ND	ND	ND	1700	None	Freon – 8.14 TCE – 0.047 cis – 0.007
30	ND	ND	ND	ND	1700	None	Freon – 3.54 TCE – 0.063 cis – 0.008
39	ND	ND	ND	ND	1900	None	Freon – 0.060
45.5	ND	ND	ND	ND	3000	Trace – Questionable	Freon – 0.065
Soil Boring SB-12							
41	ND	ND	ND	ND	NM	Trace – Questionable	ND
57	ND	ND	ND	ND	NM	None	Freon – 0.143
69.5	ND	ND	ND	ND	3000	Dark stain	Freon – 0.007
Soil Boring SB-14							
46	ND	ND	ND	ND	5000+	None	Freon – **897**
50	ND	ND	ND	ND	3700+	Dark stain	Freon – **614**
52	ND	ND	ND	ND	3300+	Dark stain	Freon – **3340**
53	ND	ND	ND	ND	NM	Dark stain	Freon – **857**
54	ND	ND	ND	ND	IND	Dark stain	Freon – **680**

Notes:

Organic vapor concentrations were measured with an OVA/FID. The value provided is the difference of the total organic vapors (unfiltered reading) minus the naturally occurring vapors (filtered reading).

mg/kg = milligrams per kilogram.

ppm = parts per million.

ND = not detected.

NM = not measured at that depth.

IND = value indeterminate because both OVA readings were off scale.

ft bls = feet below land surface.

Freon = Freon 113.

TCE = trichloroethylene.

cis = cis-1,2-dichloroethylene.

Analyte concentrations in **bold** are considered indicative of DNAPL.

Because the MIP system was relatively new at the time of the study, there is little published information available regarding its use for DNAPL delineation. Christy (1996) discusses the use of this system for monitoring organic vapors in the subsurface; however, no specific discussion regarding DNAPL delineation is made. Rossabi et al. (2000) and Kram et al. (2000) discuss briefly the use of the MIP system to evaluate DNAPL occurrence; however, no conclusions were drawn regarding its benefit or reliability.

Field Laboratory Analysis

Soil samples were collected from core intervals with elevated OVA readings and/or FLUTe liner discoloration and were submitted to a field laboratory for GC/MS analysis of VOCs. The results of these soil analyses were used to infer the presence of DNAPL, to determine the effectiveness of the various screening techniques used in the field, and to modify protocols, as indicated.

Results

Three-Dimensional High Resolution Seismic Survey

The seismic survey was successful in identifying small-scale structural features in the subsurface, as well as fracture systems within unconsolidated strata. However, little if any correlation between DNAPL occurrence and structural features was apparent at this study site. Lithologic strata in this portion of the Florida coastal plain are flat and heterogeneities are not dramatic. Study areas
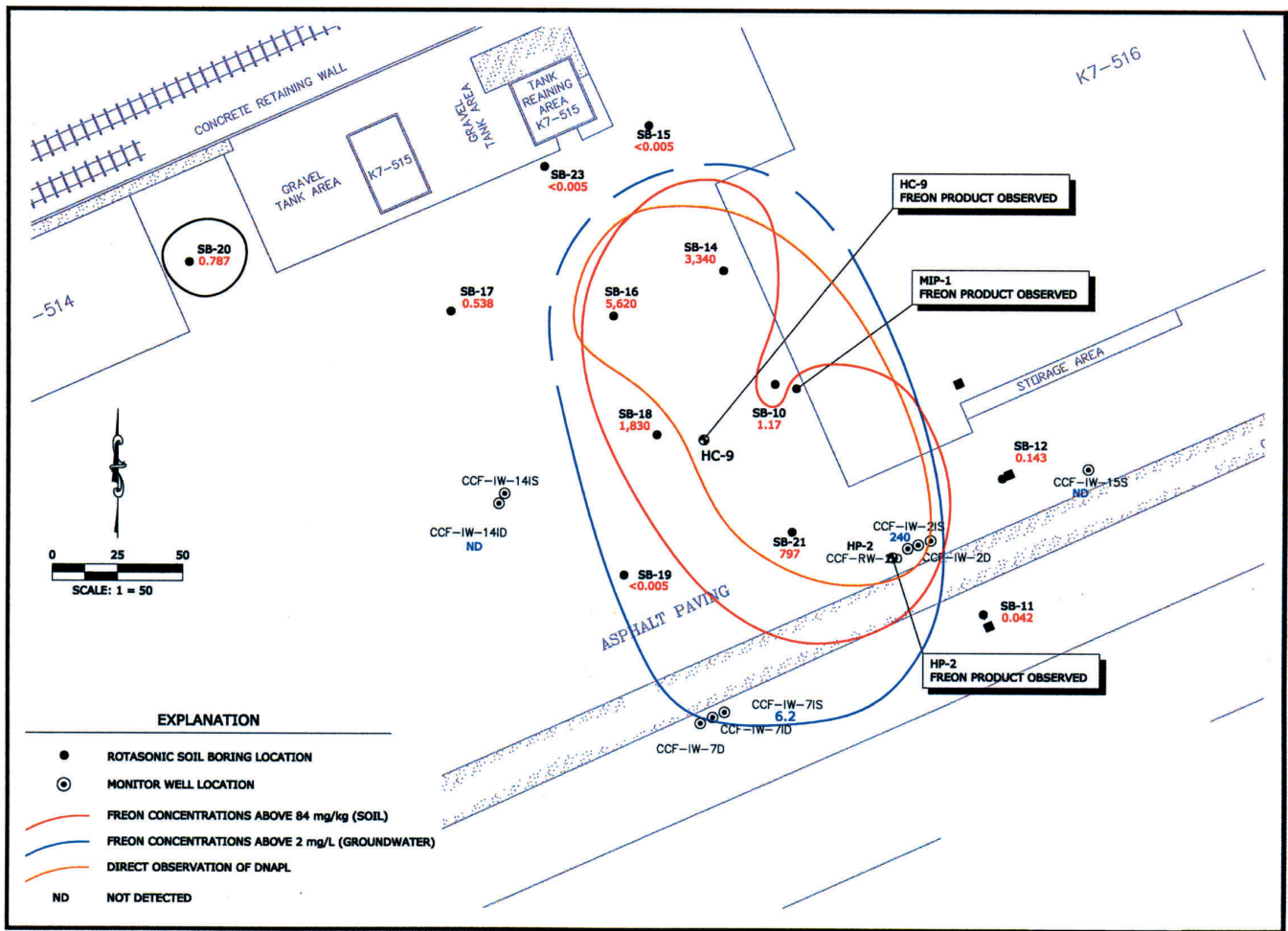
Figure 5. Freon concentrations in soil and ground water, Lab Cleaning area.

with more pronounced subsurface structures and/or fractured consolidated rock targets may benefit more from a preliminary seismic survey.

In addition to evaluation of subsurface structures, instantaneous attribute analysis of the seismic data provided no obvious evidence of seismic signal attenuation in confirmed DNAPL zones.

### Hydrophobic Dye Shake Test, Centrifugation, and UV Fluorescence

Adding hydrophobic dye to soil sample solutions and evaluating UV fluorescence was not effective in identifying DNAPL presence during this study, and these techniques were omitted after confirmed DNAPL samples provided negative results. To confirm that techniques applied in the field were performed correctly, pure TCE and Freon 113 were added to previously centrifuged samples. Two to three drops of solvent were required before significant staining and stratification were noted.

The UV fluorescence results were also difficult to interpret because most of the soil samples contained abundant shell fragments. These shell fragments appeared to fluoresce, resulting in a salt-and-pepper appearance to all samples evaluated. Therefore, minor amounts of DNAPL product (if present) could not be identified. DNAPL product was also not discernable where TCE and

Freon 113 were directly added to the sample. A representative comparison of DNAPL field test results is provided in Table 1.

Organic Vapor Analyzer Screening

Field screening for organic vapors along the length of cores provided an excellent method of focusing sample collection on impacted areas; however, results of OVA/FID readings were not always consistent with laboratory or FLUTe liner material observations. In general, OVA/FID readings exceeding about 3000 parts per million (ppm) were associated with areas where staining of reactive FLUTe liner material and/or Freon 113 was detected above a concentration of 84 mg/kg (see discussion of field laboratory analyses results). A notable exception to this was an OVA/FID reading of 400 ppm at location SB-21 with a corresponding Freon 113 concentration of 797 mg/kg (no FLUTe liner staining was noted at this location). Conversely, a number of OVA/FID readings exceeded 3000 ppm without a corresponding indication of product based on laboratory analyses or FLUTe liner reactions. At these locations, it is presumed that concentrations in ground water are near the solubility limit of Freon 113 (or TCE), or that minor amounts of DNAPL are present in residual saturation that did not come into contact with the FLUTe liners. OVA/FID readings and
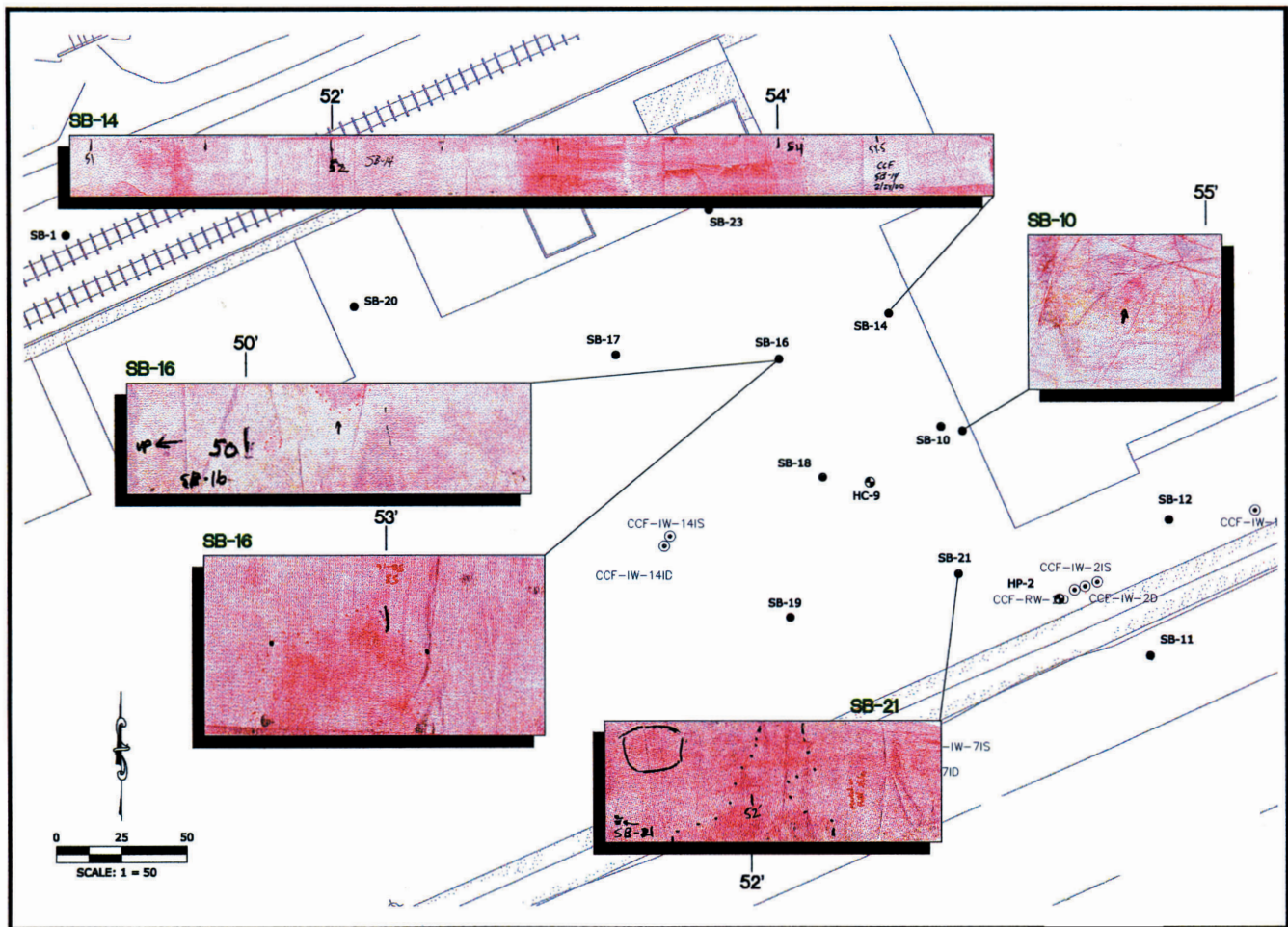
Figure 6. FLUTe liner reactions Lab Cleaning Area.
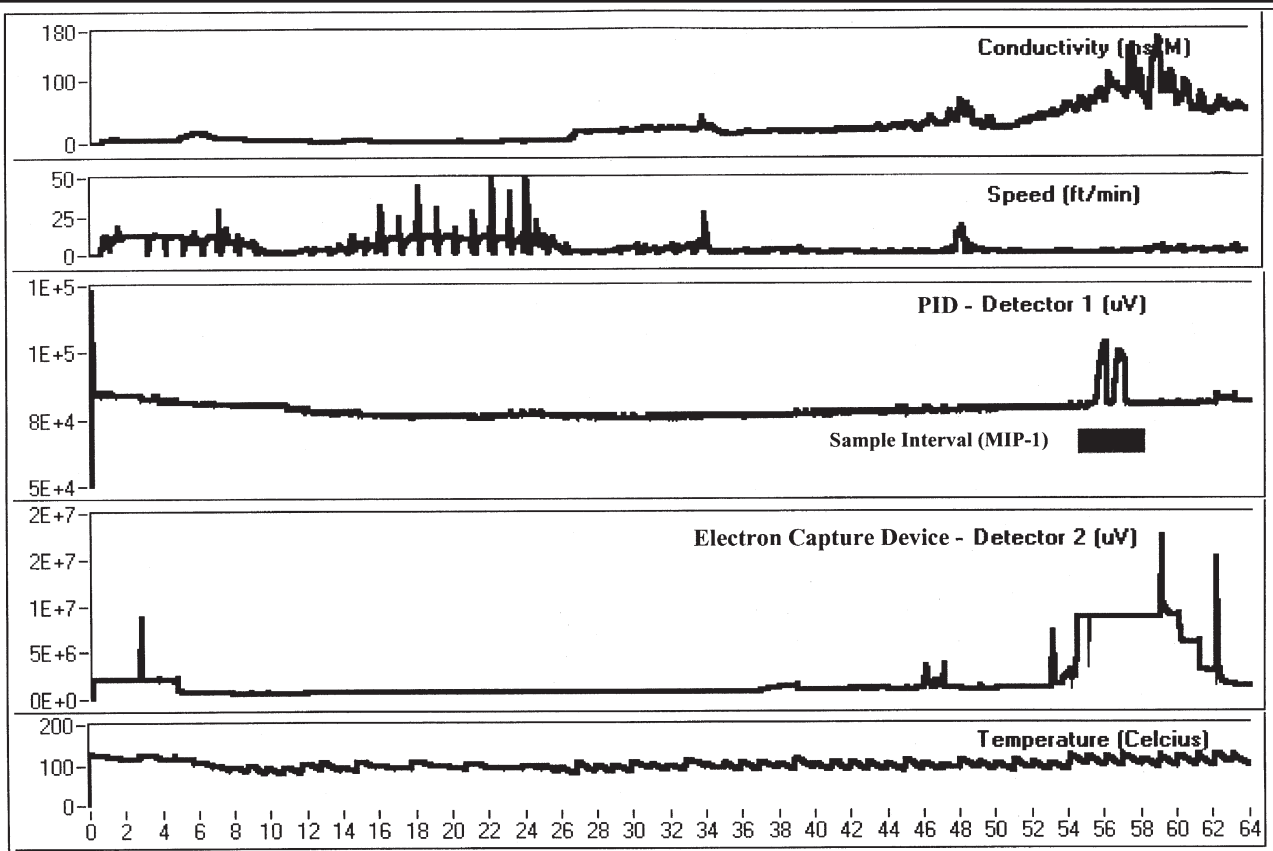
Figure 7. Membrane interface probe record (MIP-1).
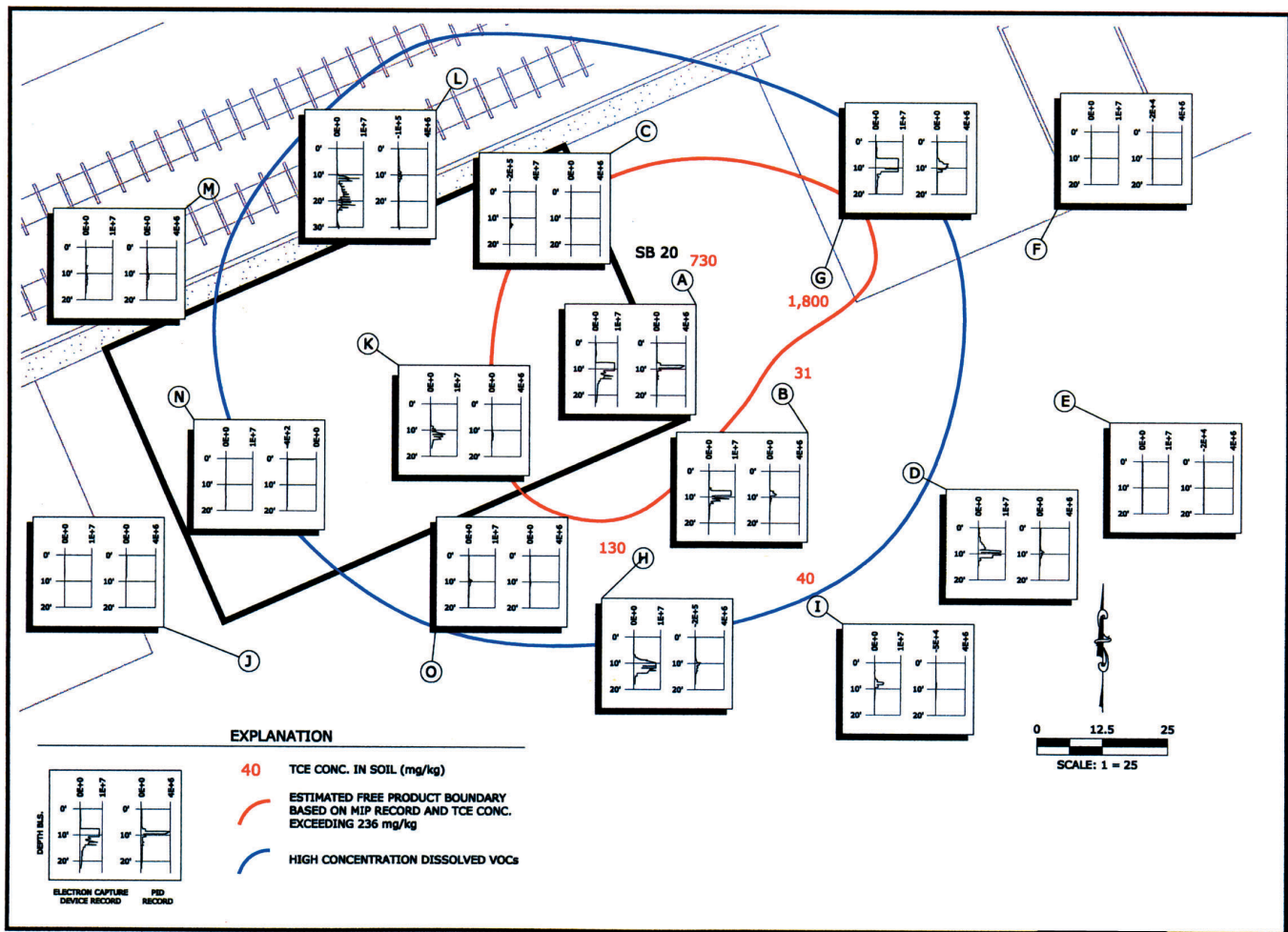
Figure 8. MIP investigation results, July 2000.

corresponding laboratory analyses of Freon 113 near the Lab Cleaning Area are shown in Figure 5. (Note: The OVA/FID relative response factors for Freon 113 and TCE are 90% and 70%, respectively.) A second smaller DNAPL area is also presented in Figure 5 around soil boring SB-20. This area is discussed further in the MIP sampling section.

Reactive Strip Evaluations

Initially, staining of FLUTe liner material was considered second only to direct observation of DNAPL fluid separation within a water sample as confirmation of DNAPL in the subsurface. DNAPL was confirmed using the FLUTe liner in several locations throughout the study area. However, minor discoloration of the liner material associated with routine handling and contact with the plastic core bags, as well as the less dramatic reaction associated with Freon 113 (compared to TCE) made interpreting select intervals difficult. Therefore, contact of small ganglia of residual DNAPL with FLUTe liner material could easily be missed. However, more substantial ganglia or pooled DNAPL should be relatively easy to observe. Additionally, it appeared that reaction with FLUTe liner material occurred fairly rapidly (within the first 30 minutes) and had a tendency to fade due to evaporation (particularly Freon 113).

Locations near the Lab Cleaning Area of the CCF site where staining was noted are shown in Figure 6. The presence of high concentrations of DNAPL was confirmed by the laboratory at all of these locations (Note: A lab sample was not collected from the SB-10 stain location). The most significant staining noted during this study occurred at sample location SB-14. In summary, the FLUTe liner was stained at all locations where DNAPL was confirmed. While minor amounts of DNAPL could be missed by this investigation technique, it provides a simple and effective means of confirming substantial quantities of DNAPL. Riha et al. (2000) reported that the Ribbon NAPL Sampler (a.k.a. the FLUTe liner material) has been the most consistently robust DNAPL characterization technique that the Westinghouse Savannah River Co. had tested. Our experience has been that staining of the liner material provides for positive confirmation of NAPL; however, an absence of staining does not provide adequate assurance that NAPL is not present, particularly in residual quantities.

MIP Sampling

An MIP system evaluation was made at only one location during the initial phase of this investigation. Before initiating the MIP boring, a small amount of

Freon 113 product was dripped onto the detector membrane at the appropriate operating temperature, and the resulting readings on both the PID and ECD were noted. The MIP record at location MIP-1 (Figure 7) provides considerable information regarding both the presence of DNAPL and the nature in which it occurs (i.e., pooled on top or adsorbed within the low-permeability unit). The depth record is included along the base of the MIP-1 record. Based on this record, a minor electrical conductivity increase occurs at a depth of about 48 feet with a second, more substantial increase occurring at a depth of about 54 feet bls. These increases indicate an increase in fine-grained soils and, presumably, a corresponding drop in hydraulic conductivity. Also occurring at these depths are increased organic vapor concentrations in the ECD record (both depths) and the PID record (deeper depth only). Additionally, the concentration increases noted on both the PID and ECD record at the deeper interval are of a magnitude indicative of free product. Based on this result, an offset Geoprobe ground water sample was collected from 55 to 59 feet bls and the sample contained phase-separated Freon 113 product beneath the water (within the 40 mL glass sample container).

In addition to identifying low-permeability unit(s) and corresponding elevated organic vapor concentrations indicative of free product, the MIP record provided insight regarding the nature of the DNAPL in situ. Specifically, the occurrence of an ECD spike slightly above the corresponding elevated conductivity reading near 48 feet bls indicates that a minor amount of free product or, alternatively, substantially elevated concentrations of dissolved-phase organics may exist immediately above this thin low-permeability lens. Alternatively, the substantially elevated concentration of organic vapors throughout the roughly 8-foot-thick low-permeability lens at 54 feet bls indicates that this unit acts more as an adsorptive sponge than an impermeable barrier on which DNAPL is pooled. This is not surprising given the relatively thin and heterogeneous nature of this low-permeability retarding unit. Based on our experience in investigating organic contamination within siliciclastic sequences within Florida and Georgia, DNAPL accumulation in the subsurface will often occur in this manner, unless the underlying confining strata are of substantially (i.e., orders of magnitude) lower hydraulic conductivity.

Based on unanticipated high concentrations of Freon 113 and TCE detected at approximately 10 feet bls in boring SB-20 (Figure 5), a second DNAPL characterization program was initiated in this area using the MIP technology almost exclusively. This study was initiated by placing TCE product on the MIP membrane and observing the resulting response on the ECD and PID detectors. The first boring was then made at the SB-20 location and a step-out approach taken from that point forward. After the TCE concentrations were sufficiently reduced in the MIP logs, soil cores were collected from select boring locations within the high-concentration depth zones. The cores were observed visually, and samples were sent to an analytical laboratory for analysis. A phase equilibrium evaluation of the soils data was used to deter-mine the TCE concentration in soil, above which free product should occur (see the "Field Laboratory Analysis" section of this paper for discussion). The calculated TCE concentration at this site was 236 mg/kg.

Interpretations of the extent of DNAPL and high-concentration dissolved VOCs at this second study area using the MIP and soil analyses are in good agreement (Figure 8). Not shown in Figure 8 are the soil conductivity records from these borings. Neither the MIP soil conductivity readings or direct observation of the cores provided evidence of textural changes at the interval in which product was encountered. Rather, a thin organic-rich layer occurred at this depth (i.e., peat, roots, etc.). Therefore, it appears that the TCE DNAPL and high concentration dissolved phase organic contamination have preferentially migrated into and within this organic-rich layer.

Field Laboratory Analysis

Field laboratory analyses of soil samples provided specific identification of the contaminants present as well as analyte quantification. Laboratory data were generally consistent with OVA/FID screening, FLUTe liner results, and MIP records; however, some minor inconsistencies were encountered. For example, at the soil boring SB-10 location (Figure 5), DNAPL was directly observed in a ground water sample, but the field laboratory analyses did not contain Freon 113 at concentrations considered indicative of DNAPL.

In addition to quantifying the analytes present, the soil analytical results were used to assess the possible presence of DNAPL. Feenstra et al. (1991) and Pankow and Cherry (1996) present a method for assessing the potential presence of DNAPL using analytical data and principles of phase equilibrium partitioning. The total concentration of a specific chemical measured in soil samples C_T (mg/L total volume) can be expressed in terms of the pore water concentration C_w (mg/L) as

$$C_T = nS_gC_g + nS_wC_w + \rho_bC_s \qquad (1)$$

where

n = porosity

S_g = volume of gas/volume of total accessible pore space in dry porous media

C_g = mass of chemical in gaseous phase at equilibrium with aqueous phase (mg/m^3)

S_w = volume of water/volume of total accessible pore space in dry porous media

ρ_b = bulk density (dry mass of soil/volume of soil [kg/m^3 or kg/L])

C_s = mass of chemical in solid phase in equilibrium with liquid phase (mg/kg)

The three terms in Equation 1 represent the mass of a chemical in a unit volume in the gaseous, aqueous, and solid phase. Substituting

$$C_g = HC_w \qquad (1a)$$

where

H = Henry's law vapor/aqueous partition coefficient

and

$$C_s = K_d C_w \qquad (1b)$$

where

K_d = $K_{oc}f_{oc}$ = solid/aqueous partition coefficient (m^3/kg)

K_{oc} = organic carbon/aqueous partition coefficient (m^3/kg)

foc = mass fraction of organic carbon in soil

Then from Equation 1,

$$C_T = (nS_gH + nS_w + \rho_bK_d)C_w \qquad (1c)$$

The total concentration per unit mass C_{soil} (mg/kg dry weight) is given by

$$C_{soil} = C_T^{NAPL} / \rho_b \qquad (1d)$$

For saturated media, $S_g = 0.0$ and $S_w = 1.0$. Equation 1c is reduced to

$$C_T = (n + \rho_bK_D)C_w \qquad (2)$$

The components of Equation 1c represent the mass of a specific chemical in the gaseous phase and bound to soil solids in equilibrium with the dissolved concentration. If C_w is set as the solubility limit of a particular chemical $C_{w,sol}$, then a measured total concentration in saturated media exceeding $C_T^{NAPL} = (n + \rho_bK_D)C_{w,sol}$ implies that the chemical is present at a higher mass than possible without free product being present.

For Freon 113 in saturated media, C_T^{NAPL} is calculated as follows:

Given that

n = 0.3 mg/L
ρ_b = 1.6 g/cm^3 = 1600 kg/m^3
$C_{w, sol}$ = 200 mg/L
K_d = $K_{oc} \times f_{oc}$ = 0.000233 m^3/kg
K_{oc} = 0.389 m^3/kg
f_{oc} = 0.0006 (obtained from unimpacted areas of the study site)

then from Equation 2,

$$C_T^{NAPL} = (0.3 + 1600 \times 0.000233) \times 200 = 135 \text{ mg/L}$$

and from Equation 1d,

$$C_{soil} = 135/1.6$$
$$= 84 \text{ mg/kg}$$

For Freon 113 NAPL to exist at this site, the total concentration must be greater than 84 mg/kg.

Once the area and general nature of DNAPL occurrence (i.e., ganglia or pools) is determined, the total amount of the contaminant in the system can be estimated using the following relationship:

$$C_T = (nS_gH + nS_w + \rho_bK_d)C_w + nS_n\rho_n \qquad (3)$$

where

$$C_T = (equation\ 1c) + nS_n\rho_n$$

and

C_T = the total mass of DNAPL
S_n = DNAPL saturation of pore volume
ρ_n = DNAPL density
C_w = dissolved concentration

Equation 3 is useful, for example, in estimating reagent volumes required for enhanced in situ remediation technologies or to compare the effectiveness of various technologies during the remediation process (visit http://gemin.getf.org/dnapl for recent Kennedy Space Center research comparing DNAPL remediation technologies).

Conclusions

Several of the techniques evaluated in this study provided positive identification of DNAPL in the subsurface. The continuous screening of cores with an OVA/FID provided reliable information regarding the presence of heavily impacted soils, helping to focus confirmation sampling activities. The FLUTe liner reactive strips provided direct confirmation of pure phase DNAPL at the site and information regarding the thickness and general character of the product in the subsurface (i.e., ganglia or pools). However, residual quantities of DNAPL may have been missed with this technique. The MIP provided rapid delineation of heavily impacted soils and allowed for accurate selection of optimal soil sample locations. The subsequent soil analytical data in combination with the MIP records provided delineation of the DNAPL area. Other techniques evaluated in this study (e.g., UV fluorescence, soil sample centrifugation, hydrophobic dye addition to soil samples) were not as useful at this study site.

A comparison of direct observation data (either FLUTe liner staining or phase-separated liquid), soil analytical data, and ground water quality data are shown in Figure 5. Three interpretations of the DNAPL area are provided as (1) a direct observation contour, (2) a 1% solubility isopleth for Freon 113 (ground water data), and (3) the 84 mg/kg isopleth based on phase equilibrium evaluations and soil data. Each of these delineation areas is in reasonable agreement; however, the best match occurs between the soil analytical data and the direct observation data. Because these areas are slightly smaller than the 1% solubility isopleth, we have concluded that the 1% solubility isopleth is a reasonable means to define the DNAPL study area; however, the other study methods provided a more accurate representation of the free product boundaries at this site.

Based on the results of this study, we conclude that the most effective strategy for identifying and delineating

DNAPL in the subsurface at a similar site would be to initially evaluate existing ground water quality data to estimate the 1% solubility isopleth boundary for the contaminant(s) in questions. The presence of DNAPL can then be confirmed and delineated using a combination of the MIP system and laboratory analysis of soil samples. The MIP study would be completed and the results evaluated prior to selecting soil core sample locations. Core samples (Rotasonic, Geoprobe, etc.) would then be collected from high-concentration intervals at these locations and the soil data evaluated with respect to phase equilibrium partitioning algorithms. After determining the analytical concentrations in soil that would be indicative of free product at the given study area, the soils and MIP data can be combined and an interpretation of the DNAPL area made.

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Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

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