DNAPL Characterization Methods and Approaches, Part 1: Performance Comparisons

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Abstract

Contamination from the use of chlorinated solvents, often classified as dense nonaqueous phase liquids (DNAPLs) when in an undissolved state, represents an environmental challenge with global implications. Mass-transfer limitations due to rate-limited dissolution can lead to long-term aquifer persistence for even small volumetric fractions. The identification of DNAPL source zones located beneath the water table is critical to ultimately achieve site remediation and aquifer restoration. This paper provides a comparison of the advantages and disadvantages of many of the methods being used for detecting and delineating DNAPL contaminant source zones. The objective is to determine which options are best to pursue based on site characteristics, method performance, and method costs. DNAPL characterization methods are grouped into approaches, which include site preparation, characterization, and data-processing activities necessary to design an effective remediation system. We compare the different approaches based on the level of chemical and hydrogeologic resolution, and the need for additional data requirements. Our findings can be used to assist with selection of appropriate site remediation management options.

Introduction

Contamination of soils and ground water by the release of dense nonaqueous phase liquids (DNAPLs), including halogenated solvents, has posed serious environmental problems for many years. To be able to remediate a site contaminated with DNAPLs, it is necessary to remove or treat undissolved (nonaqueous) product remaining in the subsurface. Failure to remove residual (held under capillary forces and essentially immobile) or free-phase (mobile) product may result in continued, long-term contamination of the surrounding ground water. The marginally soluble organic contaminants can partition into the aqueous phase at rates slow enough to continue to exist as a residual or free-phase, yet rapid enough to render water supplies a threat to public health. DNAPLs can migrate to depths well below the water table. As they migrate, they can leave behind ganglia of microglobules in the pore spaces of the soil matrix, which effectively serve as long-term sources of ground water pollution. Even at low concentrations, the solute plume emanating from DNAPL can pose a threat to human health. Current conceptual DNAPL transport models suggest that when sinking free-phase DNAPL encounters a confining layer (e.g., a competent clay or bedrock zone), it can accumulate, or "pool," and spread laterally until it encounters a fracture or an alternative path of relatively low-flow resistance toward deeper zones. In addition, globules can enter pores and be held as a resid-

ual phase in capillary suspension. This complex mode of subsurface transport results in unpredictable heterogeneous distribution of nonaqueous product that is difficult to delineate. The current lack of appropriate methods for detecting and delineating widely dispersed microglobules of DNAPL product has been identified as one of the most significant challenges limiting effective cleanup of sites contaminated with these pollutants (Feenstra et al. 1996).

This paper compares a number of approaches and methods used to detect and delineate DNAPL contaminant source zones. In addition, a cost comparison using several synthetic site scenarios will be presented in a companion article (Kram et al. 2001b). This comparison can then be used by site managers to help determine the most appropriate approach for their specific site.

A distinction between specific methods and site management approaches is necessary when comparing options. An approach, identified by a method descriptor (such as "soil gas survey" or "surface geophysics," etc.), implies a number of activities that include the specific site characterization method as part of the overall characterization effort as well as the necessary site preparation and data-processing activities, and in many instances additional characterization methods (e.g., confirmation sampling). Selected methods are grouped into approaches that represent site management options for achieving cost-effective DNAPL source zone characterization. Inherent in these characterization approaches will be the goal of identifying and quantifying lithologic and chemical site characteristics that lead to effective remediation design alternatives.

Environmental characterization efforts for contaminated sites typically evolve through a series of stages. Initially no information is available. We will refer to this stage as t_0. At t_1, some preliminary (generally nonintrusive) information becomes available that indicates the potential for risks associated with contaminant exposure. This information would include data typically contained in a preliminary site assessment. At t_2, data collection activities related to subsurface characterization are sufficient to initiate design of a remediation system. At t_3, the site is considered remediated and monitoring is established to determine whether there is further risk. At t_4, monitoring ceases and regulatory closure is achieved, thereby requiring no further action. The approaches discussed in this paper comprise multiple methods applied in a logical sequence with the goal of reaching stage t_2.

Descriptions of DNAPL Site Characterization Methods

The methods described in this section were selected because they have demonstrated potential for successful DNAPL source zone delineation at several sites. Some of the methods have been extensively tested (e.g. sample collection and analysis, soil gas surveys, seismic, and other geophysical surveys), while others are considered relatively new techniques (e.g., FLUTe, ultraviolet [UV] fluorescence using a cone penetrometer, and precision injec-

tion extraction [PIX]). Brief descriptions of the methods investigated in this effort are presented. Table 1 identifies positive and negative attributes associated with each of these characterization methods and pertinent references for obtaining additional information.

Baseline Methods

The baseline characterization method typically consists of sample collection during drilling operations. For simplicity, we consider 5-foot (1.5 m) depth intervals, without making this a recommendation. Samples are typically collected using conventional drilling equipment and are analyzed using EPA-approved methods for identifying volatile organic compounds (VOCs). Because VOCs can be rapidly liberated during handling and transport, this can lead to an underestimation of the actual concentration.

Several actions can be taken to improve the baseline method:

- Samples can be immediately immersed in methanol to inhibit the amount of volatilization due to handling and transport.
- Samples can be subject to field "shake tests" in which density differences between the relatively heavier DNAPL and water are qualitatively identified.
- Samples can be exposed to UV fluorescence with a portable meter to qualitatively identify potential fluorophores in an oil phase.
- Sudan IV or Oil Red O dye can be added to samples, which turn orange-red in the presence of NAPL, to qualitatively identify separate phases.
- Soil vapors and cutting fluids generated while drilling can be analyzed.
- Soils, fluids, and vapors within a cavity or along a trenched wall of a test pit can be analyzed.
- A small amount of soil or water can be placed in a container that is immediately sealed, equilibrated, and a sample of the vapors that have partitioned into the headspace portion in the container can be analyzed (EPA Method 5021).

The baseline method and variations previously described can be useful for identifying DNAPL source areas as long as the samples are collected from appropriate locations. Because the DNAPL may be present as extremely small globules, locating source zones with a 5-foot (1.5 m) sampling frequency can have a low probability of success. As the sampling frequency is increased, the probability of detection increases, but the cost also increases significantly. This site characterization approach may not provide sufficient information to reach the t_2 stage. Permeability tests, well installations, and evaluation of residual-phase versus free-phase product may be necessary, depending on site conditions and initial findings.

Pore water concentration can be used to evaluate whether constituent concentrations exhibited by the pore water and soil are indicative of DNAPL presence (Pankow and Cherry 1996). If the pore water concentration for a given sample is near the solubility limit of the component in water (or the estimated effective solubility of a particular component from a mixture), DNAPL is

presumed to be located within the vicinity of the sample collection location. The largest uncertainty in pore water concentration is generally caused by uncertainty in the estimate of the water-soil partition coefficient, which depends on the fraction of organic carbon content present, the octanol-water partition coefficient for the compound of interest, and complications due to unaccountable sorption, intergranular diffusion, dissolved organic matter, and cosolvency. Using equilibrium calculations, Feenstra et al. (1991) show that for soil concentrations greater than several hundred mg/kg (parts per million) TCE in a sandy soil, the majority of the component is present in the DNAPL phase. Since several components are generally present, solubility estimates are not easy to determine with a high level of certainty. In addition, ground water flow rate variations produce widely varying dissolved component concentrations adjacent to NAPL. Therefore, there is a significant need to search for direct NAPL detection methods.

Soil-Gas Surveys

Soil-gas surveys have been used successfully to screen DNAPL sites for more than a decade (Marrin 1988; Marrin and Kerfoot 1988). Soil-gas surveys consist of insertion of soil-vapor collection devices into the subsurface, most commonly using a direct-push approach, application of a slight vacuum to the soil, collection of a vapor sample, and on-site measurement of VOCs using a gas chromatograph. Because these methods can be used only in the vadose zone, they are typically used to try to identify DNAPL release areas.

Using soil-gas surveys as the main component of a site characterization approach may not be sufficient to reach the t_2 stage. Geologic profiles, permeability tests, well installations, and evaluation of residual-phase versus free-phase product may be necessary depending on site conditions and initial findings. Soil-gas survey data can help determine preferred locations for intrusive characterization methods beneath the water table.

Partitioning Interwell Tracer Tests

The partitioning interwell tracer test (PITT) is based on transport properties of several tracers, each with different partitioning characteristics (Jin et al. 1995). A forced flow field is established to transport tracers through a specific volume of aquifer investigated. A suite of tracers is introduced to the subsurface within a target DNAPL zone and recovered from a different location, typically using injection and recovery wells. At least one of the tracers is nonreactive (e.g., nonpartitioning and nonabsorbing) with respect to the DNAPL organic liquid, while the other tracers partition, to various levels, into the organic liquid. The organic liquids detain the partitioning tracers and retard their migration, thereby leading to differential recovery times corresponding to the strength of partitioning and amount of DNAPL encountered (Nelsen et al. 1999).

In practice, identification of a DNAPL zone is necessary prior to setting up the PITT using other types of characterization methods. Breakthrough curves depicting concentration versus time for a particular recovery well are generated for each tracer. The conservative, nonabsorbing tracer is initially recovered, followed by the partitioning tracers. DNAPL saturation calculations depend on determination of a retardation factor for each tracer, which is typically calculated using a comparative moment analysis with the nonreactive tracer (Jin et al. 1995).

Partition coefficient variability due to differences in NAPL composition can introduce errors in the estimation of NAPL saturation (Dwarakanath et al. 1999). It is also important to recognize that thin fractures in karst, clays, or crystalline rocks can skew the results due to random migration in fractured media (Keller et al. 2000).

An approach that includes the PITT technique requires several additional components to reach the t_2 stage (e.g., preliminary identification and location of DNAPL zones, confirmation efforts, hydrologic control, post-PITT modeling, etc.). However, because saturation volumes can be estimated, the method provides more detailed information for remedial design and evaluation of remedial effectiveness, provided the site lithology is appropriate (e.g., of medium to high permeability with low levels of organic matter).

Radon Flux Rates

Radon-222 (Rn-222) is often present as a dissolved gas in subsurface fluids. Rn-222 is a naturally occurring, chemically inert radioactive gas resulting from the decay of uranium-238. As with several of the tracers used in the PITT approach, Rn-222 has a strong preferential affinity to organic fluids relative to water. By observing a relative deficit in the aqueous Rn-222 concentration, one can surmise that partitioning into a NAPL phase has occurred (Semprini et al. 1998). The Rn-222 concentration within a NAPL-contaminated zone decreases compared to a background value as the NAPL saturation increases. Due to preferential partitioning into the NAPL phase, Rn-222 is retarded more in the presence of NAPL. According to the model, as residual NAPL saturation increases, Rn-222 concentration in the ground water adjacent to the NAPL will greatly decrease relative to the background Rn-222 concentrations. This implies high sensitivity with respect to identification of suspected DNAPL locations, whereby even small quantities of residual NAPL will lead to a significant Rn-222 deficit. Although useful as a DNAPL source zone screening and characterization method, the effect of remediation can be gauged by monitoring Rn-222 concentrations in the treatment zone. Increases in Rn-222 concentration can provide a semi-quantitative estimate of the NAPL removed.

As with the PITT method, an approach that includes the Rn-222 flux rate technique requires several additional components to reach the t_2 stage (e.g., preliminary identification and location of DNAPL zones, background radon concentration distribution and variations, possible well installations, confirmation efforts, etc.). Because Rn-222 is already present in the subsurface, there is no need to inject materials. The technique affords detailed information that can be used for remedial design and evaluation of remedial effectiveness as long as Rn-222

	Table 1		
	DNAPL Site Characterization Methods		
Methods	**Advantages**	**Disadvantages**	**References**
1a. Baseline methods: disposal witness	• Direct evidence via observation of disposal incident	• Best-guess approach for sampling location/depth • Volume not easily quantifiable • Generally small source quantities	Cohen and Mercer 1993; Pankow and Cherry 1996
1b. Baseline methods: chemical analysis of soil, rock and water samples (including fault planes in consolidated regimes)	• Direct evidence • Vertically continuous soil samples can lead to reliable identification • UV fluorescence, soil/water shake tests, shake tests with hydrophobic dyes, sponge coring, and swab tests can be used	• Lack of reliable sampling methodology • Best-guess approach for sampling location/depth and spacing • Subsample selection for analysis can be biased • Potential for loss of volatiles; • Improper collection methods can lead to vertical migration of contaminants • Drilling fluids (including air) can sometimes result in loss of DNAPLs before samples are recovered • Logistics for handling and transferring consolidated rock or cohesive clay samples can be complex	Cohen et al. 1992; Cohen and Mercer 1993; Pankow and Cherry 1996; MSE 2000
1c. Baseline methods: visual field evidence	• Direct evidence via soil and fluid centrifuge, dye enhancement, or field analytical results	• Best-guess approach for sampling location/depth • Volume not quantifiable • Small source quantities require careful cm by cm examination	Cohen and Mercer 1993; Pankow and Cherry 1996
1d. Baseline methods: enhanced visual identification: shake-tests	• Direct evidence	• Best-guess approach for sampling location/depth • Volume not easily quantifiable	Cohen et al. 1992; Cohen and Mercer 1993; Pankow and Cherry 1996
1e. Baseline methods: enhanced visual I.D.: UV fluorescence w/portable light	• Indirect evidence (commingled NAPL source)	• Best-guess approach for sampling location/depth • Volume not easily quantifiable • Can have false positives	Cohen et al. 1992; Pankow and Cherry 1996
1f. Baseline methods: enhanced visual I.D.: dye addition w/Sudan IV or Oil Red O	• Direct evidence • Excellent screening tool	• Best-guess approach for sampling location/depth • Volume not easily quantifiable • Sudan IV listed as a possible mutagen • Soil type and moisture condition may influence accuracy • Qualitative	Cohen et al. 1992; Cohen and Mercer 1993; Pankow and Cherry 1996
1g. Baseline methods: vapor analysis while sampling sediments or drilling	• Indirect evidence (while drilling or via head headspace analysis of samples) if readings of 1000 to 2000 ppm vapor (may infer DNAPL)	• Questionable vertical control • Water can skew or inhibit volatile detection • False positives due to equipment exhaust possible • Could liberate volatile constituents if sample integrity is disrupted • Semiquantitative • Drilling can lead to vertical migration of contaminants	Cohen and Mercer 1993; Pankow and Cherry 1996
1h. Baseline methods: drilling water analysis	• Indirect evidence • Can help to avoid drilling through vertical lithologic barriers	• Questionable vertical control • Concentrations can be diluted • Not quantifiably representative of subsurface conditions • Some drilling methods not capable of yielding water samples that reflect composition of ground water • Drilling can lead to vertical migration of contaminants	Taylor and Serafini 1988; Cohen and Mercer 1993; Pankow and Cherry 1996

Table 1 (continued)

Methods	Advantages	Disadvantages	References
1i. Baseline methods: observation wells	• Direct evidence if product recovered • Indirect evidence if concentrated dissolved phase constituents are detected (see Backtracking Dissolved VOC Concentrations in Wells)	• Difficult to determine DNAPL volume and vertical distribution • DNAPL may not easily flow into well, especially if present at residual saturation, or if hydraulic potential of DNAPL is insufficient to overcome capillary pressure in the filter pack • Relatively large DNAPL volumes must enter the boring to be detected in wells • DNAPLs that enter annulus may exit boring below end cap if formation is permeable leading to vertical transmission of contaminants without detection in the well • Sampling from bottom of the well can be logistically challenging	Cohen and Mercer, 1993; Pankow and Cherry, 1996
1j. Baseline methods: test pits	• Direct evidence based on observation of materials while excavating • Can be good for obtaining detailed lithologic information • Can observe relationship between DNAPL distribution and lithologic characteristics	• Difficult to determine DNAPL volume and vertical distribution • DNAPL may not easily flow into pit • Depth limited (to approximately 5 to 8 m bgs) • Can be difficult to keep pit open in saturated conditions • Potentially hazardous working conditions	Pankow and Cherry 1996
2. Soil-gas surveys	• Indirect evidence based on VOC detection in vadose zone • Very high concentrations (approaching saturated vapor concentrations) may be indicative of DNAPLs present in vadose zone adjacent to the sampling point	• Subaqueous DNAPL may not easily volatilize • Not generally depth specific due to migration characteristics of materials • Preferential pathways can lead to misinterpretation • Poor correlations between soil gas concentration and soil concentrations • False negatives possible since vapor concentrations can rapidly decline due to transport by diffusion	Marrin 1988; Marrin and Kerfoot 1988; Cohen and Mercer 1993
3. Partitioning interwell tracer tests	• Indirect evidence • Can be used for volume estimates and evaluation of remediation method efficiency	• Tracer migration may follow different pathway than DNAPL • Split flowpaths and meandering can lead to inaccurate measurements • In organic rich soils, may have partitioning into organics other than DNAPL • Inadequate tracer detection limits may lead to underestimation of NAPL saturations, especially in low permeability layers • Tracers may not partition out of solution in low permeability soils that inhibit ground water flow • Porous-media heterogeneity and variable DNAPL saturation can decrease accuracy • An inferential volume integrating estimate	Jin et al. 1995; Nelson and Brusseau 1996; Burt et al. 1998; Payne et al. 1998; Meinardus et al. 1998; Knox et al., 1998; Annable et al. 1998; Nelson et al. 1999; Dwarakanath et al. 1999; Wise 1999; Yoon et al. 1999.

Table 1 (continued)

Methods	Advantages	Disadvantages	References
4. Radon flux rates	• Indirect evidence based on aqueous Rn concentration deficits due to partitioning into organic phase • Rapid equilibration of Rn • Passive sampling (as opposed to injection) • Can assist with evaluation of remedial effectiveness	• Logistically difficult • Lack of reliable sampling methodology • Specialized sampling and analytical procedures required • Site-specific NAPL to water Rn-222 partition coefficients difficult to obtain • Best-guess aproach for sampling location/depth • Areas displaying highly variable background Rn concentrating may prove challenging • Geologic factors may lead to low correlation between Rn concentration and NAPL presence	Semprini et al. 1998
5. Backtracking using dissolved concentrations in wells	• Indirect evidence provided conditions are ideal (significant source volume; conditions conducive to impede dissolved contaminant degradation) • Spatial distribution of dissolved materials can sometimes provide information about spatial distribution of DNAPL • 10% or 1% of saturated aqueous concentration "rules of thumb" have been suggested for inferring the presence of a DNAPL phase • If ground water samples are collected in close proximity to DNAPL zones and monitoring well intake zone is comparable to the size of the DNAPL residual zone, rule of thumb dissolved concentrations can be expected • Saturated concentrations in ground water found only immediately above the source and in a thin layer at the elevation of the source in the near-downgradient area • Drive-point devices used to collect detailed vertical profiles of dissolved concentrations provide the highest probability for detecting peak concentrations • Extreme temporal variations in dissolved concentrations observed in a monitoring well may indicate that the well is located along the margin of dissolved plume	• Concentrations may not be indicative of how close to source sample was collected • Lower than 1% of effective aqueous solubility concentrations do not preclude the presence of NAPL • Active sampling, spacing of monitoring wells, and well screen length may dilute concentrations • The 1% "rule of thumb" must be cautiously applied since the dissolved plume emanating from large source zones may exhibit dissolved concentrations above 1% for a substantial distance downgradient of source • Best-guess approach for sampling location/depth • Conventional monitoring wells not likely to allow for detection of peak dissolved concentrations at DNAPL sites since well screens are generally too long, not placed in proper locations, and in insufficient quantity • Highly conductive zones can demonstrate lower concentrations in coarse-grained materials that are well flushed	Feenstra and Cherry 1988; Feenstra et al. 1991; Newell and Ross 1991; Cohen and Mercer 1993; Johnson and Pankow 1992; Anderson et al. 1992; Pankow and Cherry 1996
6. Surface geophysics	• Indirect evidence based on potential migration pathways • May provide direct evidence based on acoustic or electromagnetic contrasts provided that conditions are ideal (significant product volumes; sufficient contrasts between source area and background)	• Anomalies may not be indicative of contrasts between source area and background • Depths to suspected source zones not known without intrusive "truth-shots" • Resolution not adequate to detect ganglia on a cm scale or less • Cultural interference possible	Cohen and Mercer 1993; Pankow and Cherry 1996; Adams et al. 1998; Sinclair and Kram 1998

Table 1 (continued)

Methods	Advantages	Disadvantages	References
7. Surface geophysics	• Indirect evidence based on potential migration pathways • May provide direct evidence based on acoustic, electromagnetic, gamma, or neutron contrasts provided that conditions are ideal (significant product volumes; sufficient contrasts between source area and background, porosity and moisture content)	• Anomalies may not be indicative of contrasts between source area and background • Resolution not adequate to detect "ganglia" on a cm scale or less • Cultural interference possible • Porosity or moisture content can interfere with some methods (e.g., neutron logging)	Brewster et al. 1992; Cohen and Mercer 1993; Pankow and Cherry 1996
8a. CPT methods: permeable membrane sensor; membrane interface probe (MIP)	• Indirect evidence based on VOC partitioning into metal-polymer membrane • Can be coupled with lithologic sensors for correlation • Can use different types of detectors (FID, PID, XSD, ITMS, etc.) • Excellent screening method with good resolution • Can be deployed on smaller direct push units	• When operating with a non-continuous configuration, user required to determine appropriate depths while "on the fly," which can be difficult in zones of "ganglia" • Bulk fluids can not travel across membrane • Semiquantitative • Clogging can occur • Limited by lithology • Heat front or pressure front may inhibit membrane contact with contaminant	Christy 1998
8b. CPT methods: HydroSparge	• Indirect evidence based on VOC partitioning into carrier gas • Can be coupled with lithologic sensors for correlation • Can use different types of detectors (FID, PID, ITMS, etc.)	• User required to determine appropriate depths while "on the fly," which can be difficult in zones of "ganglia" • System purge not always rapid • Clogging can occur • Limited by lithology	Davis et al. 1997; Davis et al. 1998
8c. CPT methods: Florescence (e.g., laser induced fluorecence [LIF]) techniques	• Indirect evidence based on fluorescence of commingled materials (naturally occurring organics, multi-ring fuel compounds, etc.) • Rapid measurement in real time • Depth discreet signals • Can be coupled with lithologic sensors for correlation • Good screening method with high resolution • Can use several off-the-shelf energy sources	• Limited by lithology • False negatives and positives possible • Commingled fluorophores required • Semiquantitative, so requires confirmation samples • Not yet fully mature • Pressure or heat front may force droplets away from window	Kram 1996; Kram 1997; Kram et al. 1997; Kram 1998; Keller and Kram 1998; Kram et al. 2001a; MSE 2000; Lieberman et al. 2000
8d. CPT methods: GeoVis	• Direct evidence based on video image processing • Can be coupled with lithologic sensors for correlation • Data easy to interpret in light colored soil matrix	• Limited by lithology • Rate of data collection limited by ability to visibly process information • Transparent NAPL droplets not detectable • Pressure or heat front may force droplets away from window	Lieberman and Knowles 1998; Lieberman et al. 2000

Table 1 (Continued)

Methods	Advantages	Disadvantages	References
8e. CPT methods: LIF/GeoVis	• Direct evidence based on video image processing • Can be coupled with lithologic sensors for correlation • Data easy to interpret in light colored soil matrix • When droplets are transparent, LIF can often indirectly locate source zones	• Limited by lithology • Rate of GeoVis data collection limited by ability to visibly process information • Commingled fluorophores may be required • Transparent NAPL droplets not detectable by GeoVis • Pressure or heat front may force droplets away from window	Lieberman and Knowles 1998; Lieberman et al. 1998; Lieberman et al. 2000
8f. CPT methods: Raman spectroscopy	• Direct evidence based on Raman scatter • Fluorescence may be due to commingled materials (indirect evidence for DNAPL) • Sensitivity may be enhanced through surface coating (requires sample in contact with substrate for this configuration)	• Noncontinuous stream of data • Fluorescence due to organic materials can interfere • Detection threshold dependent upon probability of droplets appearing on sapphire window, amount of contaminants in sediment, type of sediment, soil moisture content, and degree of heterogeneity • Pressure or heat front may force droplets away from window • Detection enhancement can require longer analytical times	Mosier-Boss et al. 1997; Rossabi et al. 2000
8g. CPT methods: LIF/Raman	• Indirect evidence based on fluorescence of commingled materials (naturally occurring organics, multi-ring fuel compounds, etc.) • Rapid measurement • Depth discreet signals • Can be coupled with lithologic sensors for correlation • Good screening method with high resolution • Several off-the-shelf energy sources available • Direct evidence based on Raman scatter	• Limited by lithology • False negatives and positives possible • Semiquantitative, so requires confirmation samples • Not yet fully mature • Pressure or heat front may force droplets away from window	Kenny et al. (1999)
8h. CPT methods: electro-chemical sensor probe	• Indirect evidence based on soil vapor • 10 ppm detection levels • Sensor is small, has simple circuit requirements, low power needs, and high selectivity	• Subaqueous DNAPL may not easily volatilize • Not generally depth specific due to migration characteristics of materials • Preferential pathways can lead to misinterpretation	Adams et al. 1997
8i. CPT Methods: Waterloo (Ingleton) profiler	• Indirect evidence based on use of direct-push tool to collect aqueous samples from small-spaced ports, determine hydraulic head distribution and hydraulic conductivity distribution • Inverse model dissolved concentrations to generate concentration profiles, hydraulic conductivity versus concentration comparisons, and map distribution of percent ratio of dominant solvent species to total chlorinated compounds	• Dissolved concentrations may not be indicative of proximity to NAPL source • Concentrations lower than 1% of effective aqueous solubility do not preclude the presence of NAPL • Active sampling may affect concentrations • Best-guess approach for sampling location/depth • Highly conductive zones can demonstrate lower concentrations in well-flushed course-grained materials • Clogging can occur • Limited by lithology	Pitkin 1998; Sudicky 1986

Table 1 (Continued)

Methods	Advantages	Disadvantages	References
8j. CPT methods: cosolvent injection/extraction; precision injection/extraction (PIX) probe	• Potential direct evidence of presence of DNAPL • Can be coupled with lithologic sensors	• Difficult to insure direct contact between cosolvent and DNAPL • Density differences between cosolvent and DNAPL could pose challenges • Best-guess approach for sampling location/depth • Requires relatively long sampling times (approximately two hours or more per sample)	Looney et al. 1998; MSE 2000
9. Flexible liner underground technologies everting (FLUTe) membrane	• Direct evidence • Can be deployed using CPT • Good screening method with good resolution	• Qualitative • Requires confirmation sampling • May be difficult to apply in consolidated materials	MSE 2000

concentrations are fairly homogeneous on a local scale. For instance, sites containing radioactive waste or natural uranium deposits would not be appropriate.

Backtracking Dissolved VOC Concentrations in Wells

One method commonly used to help identify DNAPL source zones is to analyze dissolved VOC concentrations in monitoring wells. Johnson and Pankow (1992) and Anderson et al. (1992) describe the use of downgradient solute concentrations to locate DNAPL source zones through the application of physical and analytical models. The source zone location is estimated by observing the well pattern distribution, noting the localized ground water flow patterns, and backtracking upgradient against the direction of ground water flow. Computer simulations based on measured hydrogeologic properties such as hydraulic conductivity (or permeability), hydraulic gradient, and velocity can be used to generate flownets or particle tracking simulations. Flownets and particle tracking simulations may then be used to elucidate the most probable location of DNAPL source zones. Partitioning calculations comparing pore water concentrations of components to pure-phase aqueous solubility can be conducted to assess the possible presence of residual DNAPL contamination when visible evidence does not exist. While the backtracking approach is often employed in environmental investigations, it is not considered a baseline method in this paper, since monitoring wells are generally installed following conventional soil and water sampling and analysis approaches. An approach that includes the use of a backtracking technique requires several additional components (e.g., permeability tests, well installations, confirmation of DNAPL presence, evaluation of residual-phase versus free-phase product, development of a well-calibrated ground water flow model, etc.) to reach the t_2 stage.

Geophysical Surveys

Several geophysical techniques have been used to try to locate DNAPL source zones (Pankow and Cherry 1996; Adams et al. 1998; Sinclair and Kram 1998). Geophysical surveys generally are not capable of directly detecting DNAPLs, but they can assist with determination of geologic structure related to DNAPL migration pathways. These types of approaches can be separated into two main categories: surface and subsurface geophysical surveys, referring to the location of the energy source and the receivers used to interrogate the subsurface.

Surface geophysical surveys generally consist of an energy source (transmitter or impact apparatus) and receivers located at the ground surface. Energy impulses, such as electromagnetic or acoustic impulses, are transmitted to and propagated through the subsurface, either reflected or refracted off the interfaces between layers or between materials with differing signal transmission properties, and the reflected signals are received at several locations on the ground surface. In a three-dimensional survey, a grid of geophones and energy source points are configured to generate data that are sampled from a range of different angles and distances. Data can be analyzed to identify anomalies, which may represent possible pathways and traps for DNAPLs. Confirmation samples must be collected from discrete depths. Wave propagation rates (acoustic or electromagnetic) for each of the subsurface strata must be known to convert time increments to units of length.

Subsurface geophysical surveys are similar to surface geophysical surveys except that they are more intrusive in that the source and/or receivers may be located below the ground surface. As with most screening methods, confirmation drilling, sampling, and analyses are essential. Therefore, additional characterization method components will be required to reach the t_2 stage when using a geophysical technique for DNAPL source zone characterization. Spatial resolution will depend on type of method used, spacing of receivers, soil and rock type, and several additional factors. Typical resolution is on the order of meters to tens of meters, which may preclude determination of ganglia and microglobule location for most cases.

Cone Penetrometer Methods—General

Cone penetrometer (CPT) methods consist of techniques that use a direct-push apparatus to deliver the sensor probes and sampling and analytical devices to depths of interest. Lithology will dictate whether CPT methods can be used at a particular site. For the most part, CPT methods can be used at sites consisting of relatively loosely compacted, noncemented, fine- to medium-textured sedimentary deposits (ASTM 1990). Recent development of robust real-time in situ sensor technologies has revolutionized the chemical and physical site assessment arena. The level of resolution and rapid data acquisition capabilities, coupled with simultaneous technical advances in computer capabilities, have generated new ways to represent and interpret data. The current trend is to mount several sensors onto a single probe, thereby allowing for coupling of lithologic and chemical information (Lieberman et al. 1991; Lieberman and Knowles 1998). With respect to DNAPL detection, some CPT methods provide for direct quantitative detection, while others serve as screening techniques that require confirmation analyses. The following sections describe some of the most promising DNAPL detection methods that use CPT as a delivery platform.

CPT Methods—Permeable Membrane

The permeable membrane interface probe (MIP) was developed by Geoprobe Systems to allow for near real-time evaluation of subsurface volatile constituents (Christy 1998). The MIP consists of a thin composite (metal and polymer) membrane mounted along the outside of a push rod, which is in contact with a carrier gas line within the probe. The carrier gas line can be connected to several types of detectors, including flame-ionization detectors, photoionization detectors, and ion trap mass spectrometers (ITMS). The probe can be advanced with either a hammer probe or a hydraulic ram system. In practice, the MIP membrane is heated to 80°C to 125°C as it is advanced through the subsurface. VOCs present in the subsurface can partition into the membrane and migrate through it by diffusive flux. Once through the membrane, the carrier gas sweeps the VOCs to the detector. Confirmation samples will be required when using the MIP for DNAPL source zone evaluation. However, the MIP technique, when coupled with lithologic sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—Hydrosparge

The U.S. Army Site Characterization and Analysis Penetrometer System (SCAPS) Hydrosparge system integrates a customized CPT probe with a small sampling port, a sparging device, and an aboveground detector situated in the truck. The probe is advanced into the ground water to a target depth and a liquid sample is allowed to enter the sampling port. A direct sparging device bubbles inert helium carrier gas through the sample to purge VOCs. The stripped VOCs are carried to the surface for analysis using an ITMS or gas chromatograph mass spectrometer. The ITMS Hydrosparge system has

demonstrated good correlation ($R^2 = 0.87$) with EPA Method 8260 for dissolved halogenated contaminant concentrations ranging from one to several thousand nanograms per milliliter (Davis et al. 1997). Confirmation samples will be required when using the Hydrosparge probe for DNAPL source zone evaluation. However, a DNAPL source zone characterization approach incorporating the Hydrosparge probe technique, when coupled with lithologic sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—Fluorescence Techniques

Molecular absorption in the UV and visible regions of the electromagnetic spectrum is dependent on the electronic structure of the organic molecule. Absorption of energy results in the elevation of electrons from orbitals in the ground state to higher energy orbitals in an excited state. When the excited electrons cascade toward the ground state, light energy is released as fluorescence emission spectra, which can be readily measured and analyzed (Silverstein et al. 1991). Compounds consisting of double carbon bonds with weakly attached electrons (specifically, polyaromatic hydrocarbons) can be identified using low-energy bombardment techniques. Source energy will dictate which specific analytes and compounds can be detected.

Several energy sources, such as lasers and mercury lamps, have been deployed using the CPT platform. The Tri-Service SCAPS deploys a fiber-optic-based Laser Induced Fluorescence (LIF) chemical detection system, which allows for real-time, in situ subsurface detection of fuel hydrocarbon contaminants (Lieberman et al. 1991). Naturally occurring organic materials, such as humic and fulvic acids, will also fluoresce when exposed to the SCAPS laser system.

While the SCAPS LIF system is not capable of directly detecting pure DNAPLs, many of the hydrocarbon constituents SCAPS can detect are miscible with DNAPLs. These materials can become commingled before or during their introduction into the subsurface. For instance, TCE is often used to clean oil-soaked metal parts. Since petroleum hydrocarbons are miscible with DNAPLs, they can be carried to depths beneath the water table. Detection of hydrocarbons located at depths beneath the water table can assist with the delineation of DNAPLs at sites where both contaminants are present (Kram 1996). Keller and Kram (1998) have demonstrated that fluorophore (i.e., fluorescing compounds) concentrations as low as 1% in chlorinated solvent are detectable with currently available instrumentation. The SCAPS LIF system has been used to indirectly locate DNAPL source zones at several sites by identifying commingled petroleum constituents beneath the water table (Kram 1998; Kram et al. 2001a). In addition, LIF techniques have been coupled with other types of sensors (e.g., Raman, GeoVis, soil type) for analytical and visible confirmation and for identifying potential contaminant pathways. Confirmation samples will be required when using the LIF probe for DNAPL source zone evaluation. However, the LIF probe technique, when coupled with lithologic and

visible confirmation sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—GeoVIS

The GeoVis is a real-time, in situ, microscopic soil video imaging system developed by the U.S. Navy (Lieberman et al. 1998). The system consists of a miniature charge-coupled device (CCD) video camera coupled with magnification and focusing lens systems integrated into a CPT platform. Soil in contact with the probe is illuminated with an array of white light emitting diodes and imaged through a sapphire window mounted on the probe. The video signal from the camera is returned to the surface, displayed in real-time on a video monitor, recorded on a video cassette recorder (VCR), and captured digitally with a frame grabber installed in a microcomputer system. The digital image data can be incorporated into the SCAPS operation and data processing software to allow for depth-specific video clip recall. In its current configuration, the system images an area that is 2×2.5 mm, providing a magnification factor of approximately $100\times$ when viewed on a 13-inch monitor. This particular system can be advanced at a rate of approximately 4 in/min. A new system is being developed for advancing a probe capable of delivering a 5×6.5 mm image at a rate of approximately 18 in/min.

The GeoVis probe has been pushed into soils known to yield fluorescence responses using a LIF probe, generating images of DNAPL globules. In addition, the GeoVis has been combined with a standard LIF probe (Lieberman et al. 2000; Udell et al. 2000). For the GeoVis to be most successful, a recognizable color or textural contrast must exist between the DNAPL globules and the soil matrix. Confirmation samples will be required when using the GeoVis probe for DNAPL source zone evaluation. The GeoVis probe technique, when coupled with chemical and lithologic sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—LIF/GeoVis

The coupling of direct-push sensors can provide compelling evidence of the presence of DNAPL. For instance, the use of LIF coupled to the GeoVis and soil lithology sensors has been successfully demonstrated at several sites (Lieberman et al. 1998; Lieberman et al. 2000; Kram et al. 2001a). In practice, each of the sensor systems collects in situ data, which is displayed in real-time. Correlation between indirect DNAPL identification using the LIF and direct detection GeoVis information has been strong where visible contrasts between soil color and DNAPL color are recognizable, and where commingled LNAPL and DNAPL materials are present. Confirmation samples may be required when using the LIF/GeoVis probe for chlorinated DNAPL source zone evaluation. The LIF/GeoVis probe technique, when coupled with lithologic sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—Raman Spectroscopy

Raman spectroscopy relies on the detection of light wavelength shifts from compounds of interest and is capable of direct identification of several chlorinated DNAPL constituents, while fluorescence techniques are not. Raman spectroscopy is used to detect light inelastically scattered from incident radiation. Energy shifts in the scattered light are correlated to the vibrational modes of particular compounds, so compound-specific spectra are generated. The number of vibrational modes and associated energies of these modes are unique to each compound. When performing Raman spectroscopy with a monochromatic light source such as a laser, both fluorescence and scattering occur. The fluorescent signal can potentially obscure the Raman spectrum. Since fluorescence emission is fixed in wavelength, the incident light source wavelength is often altered to elucidate the Raman signal. Standard signal processing (i.e., edge detection and filtering) has also been effective at extracting the Raman signal out of a fluorescent background (Mosier-Boss et al. 1997). A Raman device has been coupled to a CPT platform and successfully used to identify subsurface DNAPL constituents by their unique spectral signatures at the Savannah River Site in Aiken, South Carolina (Rossabi et al. 2000). Although confirmation samples are not required to verify a Raman detection of DNAPL, the Raman technique may require a threshold mass fraction of DNAPL for detection. As with other strategies, confirmation samples are advised. The Raman probe technique, when coupled with lithologic sensors, can allow investigators to reach the t_2 stage.

CPT Methods—LIF/Raman

The coupling of LIF and Raman techniques into a direct push-probe has proven useful at a former drycleaner site in Jacksonville, Florida (Kenny et al. 1999). Confirmation samples will be required when using the LIF/Raman probe for chlorinated DNAPL source zone evaluation. The LIF/Raman probe technique, when coupled with lithologic sensors, will allow investigators to rapidly reach the t_2 stage.

CPT Methods—Electrochemical Sensor

Electrochemical sensors that respond to chlorine have been used to detect chlorinated hydrocarbon organic vapors in soils (Adams et al. 1997). In practice, the probe is advanced to the maximum depth of interest (generally based on probe soil sensors). Soil vapors pass through a vapor sampling port in contact with the soil and are pneumatically transported to the sensor inside the probe. Chlorine gas levels are measured as the probe is retracted to the surface. The sensor signal, calibrated on a periodic basis to allow for semiquantification, is proportional to the chlorine concentration in the vapors. Electrochemical sensors must be combined with permeability tests, well installations, and other methods to reach the t_2 characterization stage. Electrochemical sensor data can help determine optimal locations for further intrusive efforts beneath the water table.

CPT Methods—Waterloo (Ingleton) Profiler

The Waterloo Profiler, developed at the Waterloo Centre for Groundwater Research (Pitkin 1998), consists of a stainless-steel drive point with small-diameter (typically 0.156-inch) circular ports fitted with 25-mesh stainless-steel screen. The ports are each connected to a common reservoir in the tip of the profiler, which is connected to a delivery system comprising stainless-steel tubing within the profiler and a peristaltic pump at the surface. Ground water can be sampled from several discrete depths with inch-scale vertical resolution. In addition, depth-discrete aquifer testing can be conducted to generate a vertical profile of hydraulic conductivity and hydraulic head. The device has been used successfully to map DNAPL source zones by profiling in transects normal to the axis of the hydraulic gradient (Pitkin 1998). In addition, solute concentrations along transects and hydraulic head profiles have been used to "backtrack" to identify potential DNAPL source areas upgradient of the profiling regions. Confirmation samples are required when using the Waterloo Profiler for DNAPL source zone evaluation. The Waterloo Profiler technique, when coupled with analysis of depth discrete solute concentrations, piezometric head values, and estimates of hydraulic conductivity, will allow investigators to reach the t_2 stage.

CPT Methods—Cosolvent Injection/Extraction; Precision Injection/Extraction (PIX)

The cosolvent injection/extraction (or precision injection/extraction [PIX] method functions by solubilizing, mobilizing, and recovering the NAPL in contact with either a single well or a specialized probe. In practice, the probe is advanced to a target depth (or a well is packed to isolate the screen zone). A known amount of water with a conservative tracer of fixed concentration is injected a few inches into the formation and recovered by overextraction (extracting a larger volume than what was originally injected). Then a known amount of alcohol is injected and overextracted. Differences in component concentrations, alcohol concentrations, and tracer concentrations are compared to determine the potential presence of DNAPL using a mass-balance approach (Looney et al. 1998). Lithologic sensors can be incorporated to help identify candidate DNAPL zones based on potential migration conduits. This technique has been successfully implemented at the Interagency DNAPL Consortium site in Cape Canaveral, Florida (MSE 2000). Confirmation samples will be required when using the PIX technique for DNAPL source zone evaluation. The PIX technique, when coupled with relative permeability data, can allow investigators to reach the t_2 stage.

Ribbon NAPL Sampler Flexible Liner Underground Technologies Everting (FLUTe)® Membrane

The Ribbon NAPL Sampler FLUTe device consists of an inflatable membrane used to deploy a hydrophobic absorbent ribbon that is forced against the side of a borehole or penetrometer push hole in zones of suspected DNAPL contamination. If DNAPLs are present, they will wick into the ribbon. The membrane device is retracted using a tether connected to the deepest portion of the liner, and the ribbon is visually inspected and analyzed for DNAPLs (MSE 2000). Analysis consists of extraction and measurement of the concentration of contaminants adsorbed onto the ribbon, or visual review of Sudan IV dye-stained intervals. Recently, a Sudan IV-impregnated ribbon was successfully used at the Savannah River Site in Aiken, South Carolina, and at Cape Canaveral, Florida (MSE 2000; Riha et al. 2000). The membrane was deployed using a CPT. Confirmation samples may be required when using the FLUTe technique for DNAPL source zone evaluation. The FLUTe technique, when coupled with lithologic information and permeability analyses, can allow investigators to reach the t_2 stage.

Discussion and Conclusions

This paper describes and compares many of the methods and approaches currently used to detect and delineate DNAPL contaminant source zones. Specific advantages and disadvantages for several methods are presented in Table 1. Cost comparisons for various approaches using hypothetical scenarios will be published in a companion paper (Kram et al. 2001b). Perhaps the most important issue raised deals with the recognition that each candidate method must be placed in its proper context within the characterization process. The process itself is therefore considered an approach that consists of several methods, each serving to complement individual method components. It is through this recognition that a true assessment of the anticipated site management costs and project duration can be derived.

Methods described as baseline in this paper are clearly not valid for most cases. The level of resolution and detail required for site assessment and remedial design are not generally achievable using these techniques. However, these approaches can serve as confirmation efforts, provided a specific DNAPL source location is suspected based on more rigorous alternatives such as those described in this paper.

Because each method has specific advantages and disadvantages, several methods can be complementary in an overall site management plan, each serving a particular niche. This can be considered a "hybrid" approach, whereby the strengths of individual characterization components are exploited at the most appropriate and logical times in the site management process. An example characterization approach at an unconsolidated alluvium site begins with the collection of a lithologic profile followed by deployment of the direct-push FLUTe or LIF/GeoVis method, then analysis of confirmation samples. After determining the location of the DNAPL source zone, discreetly screened or multilevel wells can be installed and a Radon flux rate survey or PITT survey can be used to estimate the amount of NAPL present. For sites comprising fractured crystalline rock or karst, one can initially screen the site with a geophysical survey (including vertical profiling to convert units of time to units of

length or depth). Following the geophysical survey, the FLUTe method (deployed via drill rig) and confirmation effort can be conducted to determine the location of the DNAPL source area. Discreetly screened or multilevel wells can then be installed and a Radon flux rate survey or PITT can be used to estimate the amount of NAPL present. The number of available method combinations and potential options are extensive.

While this paper describes and compares the specific DNAPL characterization approaches, it will be up to the reader to determine which approach is most appropriate for their specific site conditions and concerns. In general, cost will most likely be the determining factor for approach selection (Kram et al. 2001b). However, several approach limitations should weigh heavily in the ultimate selection of the most appropriate site management strategy. For instance, CPT methods cannot be used in gravel or highly consolidated soils. Similarly, approaches such as soil-gas surveys and surface geophysical surveys generally require relatively more confirmation sampling due to the limited depth resolution provided by the field data. These factors, as well as others presented in this paper and in the companion cost comparison paper, should be carefully considered prior to making the financial commitment to a DNAPL characterization site management strategy.

Acknowledgments

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