United States
Environmental Protection
Agency

Ground Water Issue

Assessment and Delineation of DNAPL Source Zones at Hazardous Waste Sites

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1.0 - Introduction

Groundwater contamination from classes of chemicals such as chlorinated solvents, polychlorinated biphenyls (PCBs), creosote, and coal tar is frequently encountered at hazardous waste sites (40, 43). These types of contaminants have low solubilities in water and have densities greater than that of water. Therefore, they can exist in the subsurface as Dense, Non-Aqueous Phase Liquids (DNAPLs) and have the potential to migrate as a separate liquid phase to significant distances below the water table in both unconsolidated materials and fractured bedrock. Because of the physicochemical properties associated with DNAPLs, they migrate through the subsurface in a very selective and tortuous manner (13, 27, 29). Thus, the majority of DNAPL present in the subsurface may not be found immediately below the entry location and directly encountering DNAPLs with conventional drilling techniques may be difficult.

Determining the presence or absence of a DNAPL is an important component of the conceptual site model and is critical to the proper selection of the remediation approach. Subsurface DNAPL acts as a long-term source for dissolved-phase contamination and determines the spatial distribution and persistence of contaminant concentrations within the dissolved-phase plume. Once it has been determined that DNAPL exists within the subsurface, subsequent characterization activities are typically conducted to better delineate the boundaries of the DNAPL source zone. The DNAPL source zone is the overall volume of the subsurface containing residual and/or pooled DNAPL. It should be recognized that there will be uncertainty associated with the delineation of the DNAPL source zone. In addition to the DNAPL, there may be significant amounts of contaminant mass that have diffused into low permeability zones. Back diffusion of contaminant mass from these zones may sustain dissolved-phase plumes for significant periods of time, even after DNAPL has been removed. Establishing the presence and locations of such non-DNAPL sources is beyond the scope of this document.

In January 1992, EPA published a Fact Sheet entitled 'Estimating Potential for Occurrence of DNAPL at Superfund Sites' (42) with the goal to help site personnel determine if DNAPL-based characterization strategies should be employed at a particular site. In September 1994, EPA issued a subsequent Fact Sheet entitled 'DNAPL Site Characterization' (39) discussing direct and indirect methods to assess the presence of DNAPL in the subsurface. Since the publication of the initial fact sheets, there have been advancements in characterization tools, site investigation approaches (14) and knowledge of DNAPL source zone architecture within the subsurface. This document builds on information from the previous fact sheets to provide a framework for not only assessing the presence of DNAPL, but also for delineating the spatial extent of the DNAPL source zone, a priority at many sites due to the more prevalent use of *in-situ* remediation technologies (38). The strategy described in the present document utilizes converging lines of evidence that incorporate the scientific advancements in the field and expands the applicability of the document to include both unconsolidated deposits and fractured bedrock. An iterative, flexible site investigation approach (7) is encouraged.

2.0 - Nature of the DNAPL Source Zone

Upon release to the subsurface, DNAPL will distribute itself in the form of disconnected blobs and ganglia of organic liquid referred to as residual DNAPL, and in connected distributions referred to as pooled DNAPL (Figure 1). Residual DNAPL is found both above and below the water table within the pathways of DNAPL migration, and typically occupies between 5% and 30% of pore space in porous media (6, 27, 44) and in rock fractures (21). Residual DNAPL is trapped by capillary forces, and typically will not enter an adjacent monitoring well, even under the influence of aggressive groundwater pumping (6, 27).

Pooling of DNAPL can occur above capillary barriers, which are typically layers and lenses of slightly less permeable material (Figure 1). Pooling can therefore occur at any elevation in the subsurface, and not just at the base of permeable zones. Absence of pooling above clay aquitards and bedrock may be due to the presence of dipping fractures, bedding planes, joints and faults which may allow the continued downward migration of the DNAPL. Pools represent a continuous distribution of DNAPL, and typically correspond to DNAPL saturations of between 30% and 80% of pore space in both porous media and fractures. The frequency of pool occurrence and the thickness of pools are increased by the presence of horizontal capillary barriers, lower DNAPL density, higher interfacial tension, and an upward component to groundwater flow (17, 22). The thickness of pools typically ranges from fractions of an inch to a few feet, depending on fluid and media properties (36) as well as the volume released. Because pools represent a connected distribution of DNAPL, the pooled DNAPL is susceptible to mobilization through drilling activities and can short-circuit along existing monitoring wells and piezometers. In addition, pools may also be mobilized in response to changes in hydraulic gradient. The gradient required to mobilize a pool is a function of the DNAPL-water interfacial

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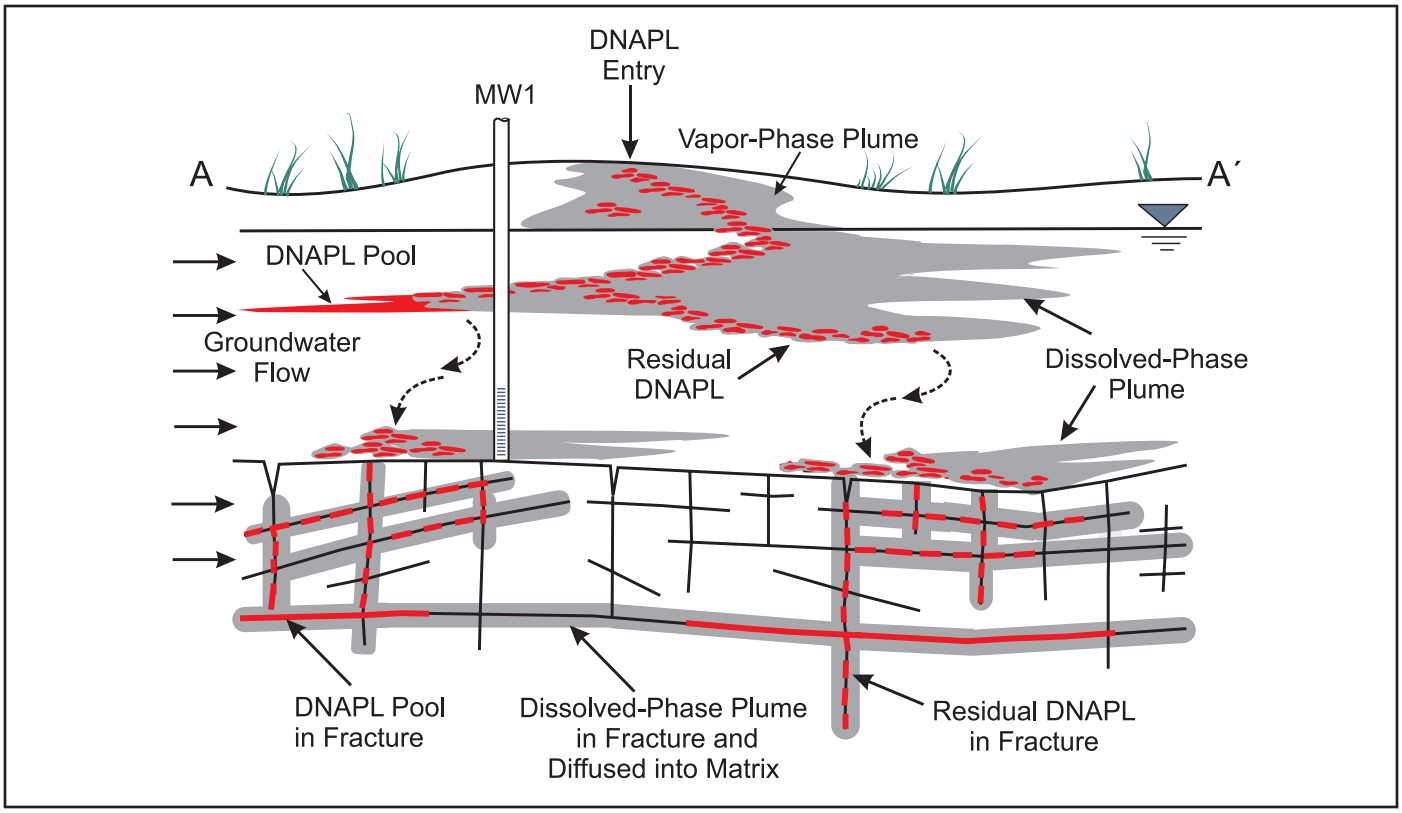

Figure 1 – Schematic illustration of contamination associated with a DNAPL release. Note that DNAPL migrates in three dimensions, and that residual DNAPL accumulated above bedrock is the result of the release at ground surface. The reader is referred to Figure 2 for a depiction of matrix diffusion. Figure is not to scale.

tension, the pool length, and the permeability of the surrounding material (6, 27). Pumping groundwater from beneath DNAPL pools, for example, can lead to an increase in capillary pressure and subsequent downward DNAPL mobilization.

The spatial distribution of residual and pooled DNAPL is strongly influenced by geology, and also by DNAPL properties and release history (frequency, intensity, duration, volume and location). DNAPL migration can occur through lenses and laminations of porous media at the scale of inches or less (17, 29). For DNAPLs that are non-wetting (see wettability in glossary) with respect to water (which is usually the case), migration below the water table is typically through the larger pores (and hence higher permeability regions) in unconsolidated media and larger aperture fractures in bedrock. The orientation of stratigraphic and structural features will largely determine the degree of lateral and vertical DNAPL spreading. DNAPL migration from the release location can occur in any direction, and is typically not greatly influenced by low ambient hydraulic gradients except for creosotes and coal tars which have densities close to that of water.

The overall region of the subsurface containing residual and pooled DNAPL is referred to as the DNAPL source zone. For high density and low viscosity DNAPLs (such as chlorinated solvents), migration in relatively permeable media can cease as soon as a few months to a few years following the time of release (3, 17, 27, 29). Some geological conditions, such as horizontal to sub-horizontal fractures, gently dipping strata and sand seams in low permeability media can give rise to longer time scales for migration of chlorinated solvent DNAPLs, particularly for large volume DNAPL sources. For low density and high viscosity DNAPLs (such as creosote and coal tar), migration has the potential to continue for many decades (12). The overall depth of DNAPL migration is dependent not only on the presence or absence of capillary barriers, but also on the volume released, the interfacial tension, the degree of lateral spreading, and the bulk retention capacity (see glossary) of the medium. Because fractured rock has very low bulk retention capacity, small volumes of DNAPL can migrate greater distances in bedrock in comparison to the same volume released into unconsolidated deposits (18).

Groundwater flowing past residual and pooled DNAPL will result in dissolved-phase plumes of contamination. Complete dissolution of all DNAPL as a result of natural groundwater flow is expected to take from several decades to hundreds of years for most DNAPLs. For multi-component DNAPLs, the presence of more than one component typically suppresses the aqueous solubility of the other components in the DNAPL (6, 27). Exceptions to this can occur, however, when co-solvents such as alcohols are present in the DNAPL. In the absence of co-solvents, the concentration of any particular component dissolving into groundwater can often be approximated using Raoult's Law (2, 6, 27). Early in the dissolution process, the plume chemistry will be dominated by the higher effective solubility components which tend to be those present in the largest mass fraction within the DNAPL, and those

with the highest single-component (handbook) solubility values (24). The concentration of any or all components in groundwater downgradient of a multi-component-DNAPL source zone will typically be lower than expected using a single component solubility limit. With time, both the DNAPL composition and the plume composition will change in response to the dissolution process. The dissolved components that comprise the plume will migrate in groundwater subject to advection, dispersion, sorption, volatilization, and degradation processes.

Both residual and pooled DNAPL, and dissolved-phase plumes that are in direct contact with clays, silts, or a porous bedrock matrix, can diffuse into the low permeability media (forward diffusion). If concentrations outside of the low permeability zone become lower than those inside, diffusion will occur back into the higher permeability zone (back diffusion) and can result in plume persistence (5, 33). The forward and back diffusion processes are collectively referred to as matrix diffusion (Figure 2). The persistence of DNAPL in fractures in bedrock, saprolite and clay can be shortened by the matrix diffusion process (19, 28). In addition, the rate of advance of a dissolved-phase plume in fractured rock with a porous matrix can be strongly attenuated by the matrix diffusion process (20, 35). The influence of matrix diffusion on dissolved-phase plume migration in fractured rock and clay relative to other processes such as advection, dispersion, sorption, and possible degradation processes will vary depending on site specific geological conditions and contaminant properties. In general, matrix diffusion has a greater influence on dissolved-phase plume migration in the case of wider fracture spacing, smaller fracture aperture, lower hydraulic gradient, higher matrix porosity, and higher matrix organic carbon.

Above the water table, volatile DNAPL can vaporize into air filled pore spaces (Figure 1). For DNAPLs with significant vapor pressure, this can lead to expanded vapor-phase plumes in the unsaturated zone. The concentration of contaminants in the vapor phase will be governed by the vapor pressure, and for a multi-component DNAPL can often be approximated using Raoult's Law. In relatively warm and dry environments, the persistence of some DNAPLs (e.g., chlorinated solvents) can be relatively short (on the order of months to a few years) in unsaturated media. The absence of residual and pooled DNAPL in the unsaturated zone may not, therefore, be sufficient evidence to conclude that DNAPL has not migrated below the water table at the site of interest.

3.0 - Types of DNAPLs

Coal Tar is a complex mixture of hydrocarbons produced through the gasification of coal that was produced as a by-product of manufactured gas operations as early as 1816 in the United States. It is still produced as a by-product of blast furnace coke production. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene oil, and pitch. The low density (typically 1.01 g/cc to 1.10 g/cc

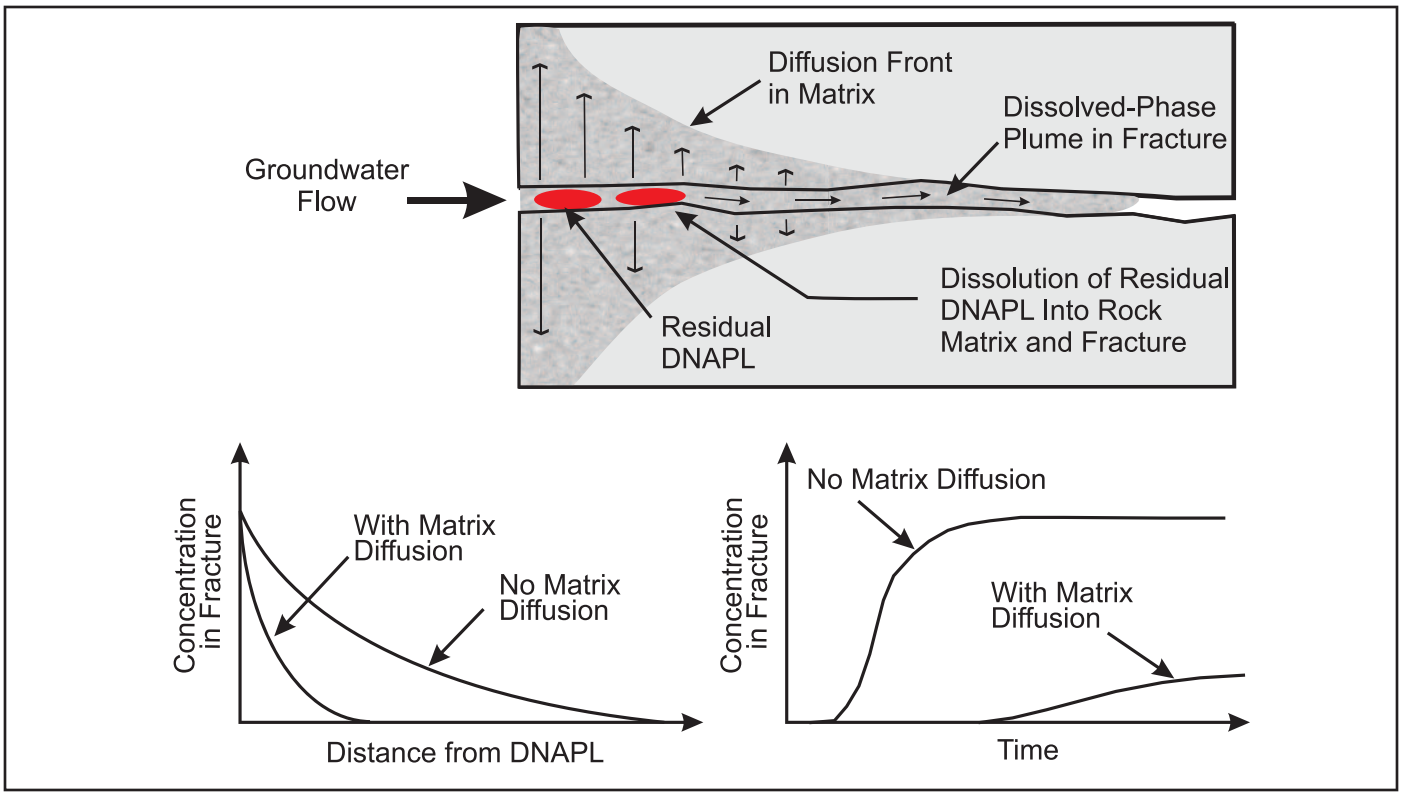

Figure 2 – Matrix diffusion of dissolved-phase contaminants adjacent to DNAPL and along length of plume in fracture. Matrix diffusion can attenuate the rate of plume advance in fractured rock (bottom left concentration vs distance plot), and can result in delayed breakthrough curves (bottom right concentration vs time figure). These factors need to be considered when relying upon groundwater concentration data to assess DNAPL presence.

compared to 1.00 g/cc of water [at 4°C]) and high viscosity (up to 200 to 300 times, or more, than that of water) facilitate long time-scales of migration, with the possibility of movement continuing for many decades following initial release. Due to the lengthy list of compounds present in coal tar, many investigators select a sub-set of coal tar compounds based on mobility and toxicity to assess water quality. These compounds may include benzene, toluene, ethylbenzene, xylenes (BTEX), benzo[a]pyrene, naphthalene, and phenanthrene. Depending on the age of the DNAPL and groundwater velocity, some of the lower molecular weight and more soluble compounds of the coal tar may have been leached out of the DNAPL by the time a site investigation is initiated. Naphthalene is often the dominant compound in present day coal tar (9). In addition, the various components in the plume will migrate at different velocities because of varying degrees of sorption and degradation (often aerobic conditions). The lower molecular weight, less sorbing compounds (e.g., BTEX) can migrate significantly further in groundwater than the higher molecular weight, more sorbing compounds (e.g., PAHs).

Creosote is composed of various coal tar fractions and was commonly used to treat wood products. It is still used today in certain wood treating operations and as a component of roofing and road tars. Creosote is a multi-component DNAPL that contains many hydrocarbons, primarily polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, and carrier fluids such as diesel. The low density (typically 1.01 g/cc to 1.13 g/cc) and high viscosity (typically 20 to 50 times that of water) of creosote facilitate long time-scales of migration, with the possibility of movement continuing for many decades following initial release. Most investigators select a sub-set of creosote compounds, based on mobility and toxicity to characterize water quality, such as naphthalene, benzo(a)pyrene, and phenanthrene.

Polychlorinated Biphenyls (PCBs) are a class of 209 chemical compounds referred to as congeners, in which between one and ten chlorine atoms are attached to a biphenyl molecule. The majority of PCBs were manufactured between 1930 and 1977 under the trade-name Aroclor for use in capacitors, transformers, printing inks, paints, pesticides, and other applications. Aroclors differ based on the amount and types of congeners present. PCBs by themselves are DNAPLs, and were often blended with carrier fluids such as chlorobenzenes and mineral oil prior to distribution. The density of most PCB oils ranges from 1.10 g/cc to 1.50 g/cc, while the viscosity ranges from 10 to 50 times that of water. Most congeners are very hydrophobic and their transport can be retarded strongly relative to the rate of groundwater migration. In some cases, however, PCB transport in groundwater can be facilitated through the formation of emulsions or the presence of colloids.

Chlorinated Solvents such as trichloroethene (TCE), tetrachloroethene (PCE) and carbon tetrachloride (CT) have been produced in large quantities since the mid 1900's. Some chlorinated solvents contain trace amounts of stabilizers, preservatives and impurities. Typical uses vary widely and include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation, and chemical intermediates. Chlorinated solvents can be encountered as single component DNAPLs (e.g., as primarily PCE at a dry cleaning facility, or as primarily TCE at a vapor degreasing facility), or as part of a multi-component DNAPL containing other organic compounds. The relatively high density (typically 1.10 g/cc to 2.20 g/cc) and low viscosity (typically ranging from half to twice that of water) of chlorinated solvents can result in a relatively short time-scale of migration following release compared to coal tar and creosote. In a dissolved-phase plume, most chlorinated solvents are not retarded strongly relative to the rate of groundwater flow.

Mixed DNAPLs A DNAPL that contains two or more compounds is referred to as a multi-component DNAPL (e.g., creosote). A mixed DNAPL is a multi-component DNAPL that contains a wide variety of organic compounds as a result of blending and mixing prior to disposal operations, or as a result of cotemporaneous disposal. Examples include DNAPLs encountered at former solvent recycling facilities and industrial disposal sites. Such DNAPLs can contain aromatic compounds normally associated with LNAPLs (e.g., toluene) along with chlorinated solvents, PCBs, alcohols, ketones, and tetrahydrofuran. The density of mixed DNAPLs typically ranges from 1.01 g/cc to 1.60 g/cc, and the dissolved-phase plumes associated with mixed DNAPLs usually contain a wide variety of compounds with varying mobility.

4.0 – DNAPL Source Zone Investigation Methods

This section presents various site investigation methods and related interpretation techniques that can be useful when characterizing a DNAPL source zone. These methods and techniques will be relied upon in Sections 5 (Assessing DNAPL Presence) and 6 (Delineation of the DNAPL Source Zone). Additional information is provided in (6, 26, 37).

A Visual Observation

DNAPL obtained from the bottom of a monitoring well or as an emulsion from a pumped water sample is conclusive evidence of DNAPL presence (pooled DNAPL). Monitoring wells can be sampled for DNAPL using bottom loading bailers lowered to the bottom of the well or pumping from the bottom of the well. If an interface probe indicates DNAPL presence, then the sample should be retrieved and it should be confirmed (visually, or through laboratory analysis) that the substance is DNAPL. If DNAPL is visually observed in drill cuttings or in a soil sample for the first time, then a sample should be sent to the laboratory for confirmatory evidence. This line of evidence is applicable in both unconsolidated deposits and fractured rock, but it should be noted that visual observation of DNAPL in rock core is rare because of the aggressive flushing nature of the drilling process. Because of the typically sparse and tortuous nature of DNAPL distribution in the subsurface, DNAPL is not encountered and visually observed within many DNAPL source zones.

B Chemical Concentrations in Soil Above Threshold DNAPL Saturation

Chemical concentrations in soil exceeding the value corresponding to a threshold DNAPL saturation are conclusive evidence of DNAPL presence (see Calculation 1). The threshold DNAPL saturation for use in Calculation 1 should be set to be between 5% and 10% of pore space for all DNAPL types. The particular threshold satura-

tion chosen should result in a chemical concentration in soil that is an order of magnitude higher than that determined in line of evidence C. It follows that high organic carbon content soils and highly hydrophobic chemicals may require the use of threshold saturations toward the higher end of the above range. This method is applicable to unconsolidated media both above and below the water table, but is not applicable in fractured rock. The calculation requires knowledge of site-specific parameters and a quantitative chemical analysis of the soil. Care should be taken to sample soil horizons in core exhibiting the highest headspace readings and the strongest visual indication of DNAPL presence. The use of fixed depth intervals or compositing from several depth intervals is discouraged when collecting soil samples to evaluate the presence of DNAPL. Methanol preservation or a similar technique to reduce VOC losses during handling and transport of soil samples should be employed.

C Chemical Concentrations in Soil Above Partitioning Threshold

Chemical concentrations in soil exceeding the value corresponding to equilibrium partitioning relationships (see Calculation 2) are consistent with DNAPL presence (11). The composition of the DNAPL need not be known (see Calculation 4). The calculation is applicable to unconsolidated media both above and below the water table, but is not applicable in fractured rock. The calculation requires knowledge of site-specific parameters and a quantitative chemical analysis of the soil. Measured concentrations that only marginally exceed the calculated partitioning threshold may be false positives primarily because of uncertainty associated with estimating the soil-water partition coefficient.

D Site Use/Site History

Investigations during the past 30 years have shown that the subsurface occurrence of DNAPL is often associated with the industries, practices, and processes outlined in Table 1. Site Use/Site History can be ascertained using methods such as employee interviews, company purchase and sale records, aerial photographs, and building plans. Former lagoons, underground tanks, floor drains and leach fields are sometimes coincident with the location of DNAPL source areas.

E Vapor Concentrations

The location of a vapor-phase plume may be coincident with the current or former presence of DNAPL in the vadose zone. Mapping the vapor-phase plume may be useful in deciding where to collect additional data. Because some DNAPLs can completely vaporize in relatively short time periods (yet the vapors will persist much longer), the presence of vapors and the mapping of a vapor-phase plume should generally not be used in isolation to conclude that DNAPL is present in the vadose zone, or to delineate the spatial extent of the DNAPL source. Care should also be taken to avoid mistaking vapors derived from off-gassing of a groundwater plume with vapors derived from DNAPL sources. In-situ vapor concentrations can be sampled using invasive techniques (soil vapor surveys), and can be monitored during drilling. This line of evidence is not applicable to DNAPLs lacking a significant vapor pressure (e.g., coal tar, creosote, PCBs).

F Hydrophobic Dye Testing

Hydrophobic dyes such as Oil Red O will partition into DNAPL, imparting a red color to the organic liquid. Dye techniques are particularly useful when encountering a colorless DNAPL. Hydrophobic dye techniques include the jar shake test in which a soil or water sample is placed into a jar with a small amount of dye (6), and down-hole samplers that force a dye-impregnated absorbent ribbon against the borehole wall in either fractured rock or a direct push borehole (30). It should also be noted that the absence of staining on a down-hole ribbon sampler is not evidence of the absence of DNAPL, since only pooled DNAPL can migrate towards the sampler (residual DNAPL may be present in the formation adjacent to the sampling interval, and remain undetected).

Table 1 – Industries and Industrial Processes Historically Associated With DNAPL Presence (modified after USEPA, 1992).

Industry	*Industrial Process*
Manufactured gas plant, Wood preservation (creosote), Electronics manufacturing, Solvent production/recycling, Pesticide/Herbicide manufacturing, Dry cleaning, Instrument manufacturing, Metal product manufacturing, Engine manufacturing, Steel industry coking operations (coal tar), Chemical production, Airplane maintenance, Transformer oil production	Storage of solvents in uncontained drum storage areas, Metal cleaning/degreasing, Metal machining, Tool and die operations, Paint stripping, Use of vapor and liquid degreasers, Storage and transfer of solvents in above and below ground tanks and piping, Burning waste liquids, Storage and treatment of waste liquids in lagoons, Use of on-site disposal wells, Loading and unloading of solvents, Transformer reprocessing, Disposal of solvents in unlined pits.

The following lines of evidence G1 through G6 all make use of groundwater quality data and can be evaluated every sampling round.

G1 Magnitude of Groundwater Concentrations

Sampled groundwater concentrations in excess of 1% effective solubility (see Calculation 3) indicate that the sampled groundwater may have come in contact with DNAPL. If the composition of the DNAPL is not known, Calculation 6 can be used. The distance to the possible DNAPL locations cannot be determined from the magnitude of the concentration alone. Sampled groundwater concentrations downgradient of a DNAPL source zone can be significantly less than the effective solubility because of hydrodynamic dispersion, wellbore dilution, non-optimal monitoring well placement, and degradation processes. In cases where significant degradation is occurring in the dissolved-phase plume, daughter product concentrations can be converted to equivalent parent product concentrations before comparing to the 1% effective solubility threshold (see Calculation 8). However, it should be noted that daughter product compounds may also be part of a multi-component DNAPL. Monitoring well points where groundwater concentrations exceed 1% effective solubility can also be useful in locating additional sampling points potentially nearer to the possible DNAPL source zones. The interpretation of groundwater concentrations exceeding 1% effective solubility is discussed further in (27).

G2 Persistent Plume

The presence of a contiguous and persistent plume extending from suspected release locations in the downgradient direction is evidence of a continuing source (e.g., DNAPL). If 'sufficient time' has passed since the last possible introduction of contaminant to the subsurface and the plume has not 'detached' itself from the suspected release locations, a DNAPL source may be present. The 'sufficient time' is dependent on site-specific conditions such as groundwater velocity and the amount of sorption occurring (see Calculation 7). This line of evidence is applicable to both unconsolidated deposits and fractured rock, but can be inconclusive in environments subject to significant amounts of back diffusion (e.g., fractured bedrock with a porous matrix, fractured clay). Significant amounts of back diffusion can be the source of a persistent plume even if DNAPL is not present. This line of evidence is therefore most applicable to high permeability settings.

G3 Presence of Contamination in Apparently Anomalous Locations

The presence of contaminated groundwater in locations that are not downgradient of known or suspected sources may be evidence of DNAPL presence hydraulically upgradient of the monitoring point in question. An example includes the presence of dissolved-phase contamination in groundwater that is older than the potential contaminant release (using age dating) or in groundwater on the other side of a flow divide located between the monitoring location and suspected release locations. In Figure 1, for example, the presence of contamination in the illustrated monitoring well cannot be explained without the upgradient presence of DNAPL. This line of evidence is not contingent on any concentration threshold. Temporal changes in hydraulic heads and groundwater flow directions, as well as changes in historic pumping patterns should be considered at sites where groundwater extraction has, or is, occurring. Consideration should also be given to the presence of unknown or off-site sources that may account for the observed contamination.

G4 Groundwater Concentration Trends with Depth

Abrupt reversals of groundwater contaminant concentration levels with depth or increasing concentrations with depth can be associated with DNAPL presence. Concentration trends can be best detected using small interval sampling techniques [e.g., direct push sampling devices; short well screens; multilevel completions; cone penetrometer equipped with measurement probes (16, 26)]. Multilevel monitoring completions can be incorporated into open holes in bedrock to provide concentration as a function of depth. Other methods in bedrock include the use of temporary straddle-packer assemblies to sample specific depth intervals, and the use of diffusion bag samplers placed at specific depths. Use of these latter methodologies should be made only when intraborehole flow conditions have been adequately characterized.

G5 Groundwater Concentration Trends with Time

Groundwater downgradient of a multi-component DNAPL may exhibit a temporal decline in the concentration of the higher effective solubility compounds and a stable or increasing trend in time of the lower effective solubility compounds. Highly soluble and mobile compounds, such as low molecular weight alcohols, furans, ketones and some solvents such as methylene chloride may show a decreasing concentration versus time signature downgradient of a DNAPL source zone while at the same time higher molecular weight alcohols and semi-volatile compounds may show a stable concentration trend. This line of evidence is primarily applicable to mixed DNAPLs. Consideration should be given to compound specific biodegradation, which may result in the concentration of certain compounds decreasing and others (such as low molecular weight daughter products) increasing within the plume. Dissolved-phase concentrations downgradient of a single component DNAPL may decline due to removal of some of the source mass during dissolution; a declining concentration versus time signature does not preclude the presence of DNAPL.

G6 Detection of Highly Sorbing Compounds in Groundwater

The detection of highly sorbing and low solubility compounds which have low mobility in groundwater may be

associated with a nearby DNAPL source. This line of evidence can be useful in delineating the extent of the DNAPL in the downgradient direction. Examples of compounds that have very low mobility in groundwater (absent transport facilitated by colloids, cosolvents, or emulsions) include PCBs and high molecular weight PAHs.

H Other Types of Methods

Partitioning interwell tracer tests (PITTs) [1, 4, 15] involve the injection and withdrawal of a tracer that has the ability to partition into the DNAPL. While the method can be used to detect the presence of DNAPL, given the significant effort involved in conducting tracer tests, PITTs are typically employed after some level of source zone characterization has been completed. Literature sources suggest (for certain sites with appropriate geologic conditions and contaminant properties) measuring a depletion of Radon-222 in groundwater (34). Direct push platforms can be used to deploy a variety of probes to vertically profile contaminant concentrations. These probes include laser induced fluorescence (LIF) measurement devices (6, 31, 32) such as ROST (rapid optical screening tool) and TarGOST (tar-specific green optical screening tool), which is specifically designed for detecting the presence of coal tar and creosote (32); and probes employing Raman methods (31). LIF techniques respond well to the presence of NAPLs containing aromatic hydrocarbons, but may not be suitable for many chlorinated solvent DNAPLs. Direct push platforms can also be used to deploy a membrane interface probe (MIP) or a hydrosparge probe (8), both of which transfer contaminants to a flowing gas stream for analysis at the surface. Another measurement probe is the precision injection/extraction (PIX) device (23). The use of measurement probes with direct push platforms is becoming increasingly popular, but care should be taken in interpreting results with respect to DNAPL presence given that most of these devices provide a relative measure of total concentration. Consideration of the potential for, and consequences of, false positives should be given to each of these methods.

5.0 - Assessing DNAPL Presence

Determining the presence or absence of DNAPL is an important component of the site characterization process and subsequent development of a conceptual site model. The length of time and degree of effort required to determine the presence or absence of DNAPL will vary from site to site. Once it has been determined that DNAPL resides in the subsurface, the objectives for further investigation and potential remediation strategies can be established. This section focuses on methods to assess the presence of DNAPL; Section 6 of this document focuses on methods to delineate the DNAPL source zone.

Converging lines of evidence can be used to determine whether or not DNAPL is present in the subsurface. Figure 3 presents a graphical summary of the converging lines of evidence approach. Example calculation procedures are contained in Appendix A. All lines of evidence are discussed in Section 4, and are applicable to both unconsolidated deposits and fractured rock, unless noted otherwise. As indicated in Figure 3, either line of evidence A or B will lead to the conclusion that DNAPL is present. If A and B are both found to be negative, then the determination of whether DNAPL is present must be made on the basis of a weight of evidence approach, with multiple converging lines of evidence

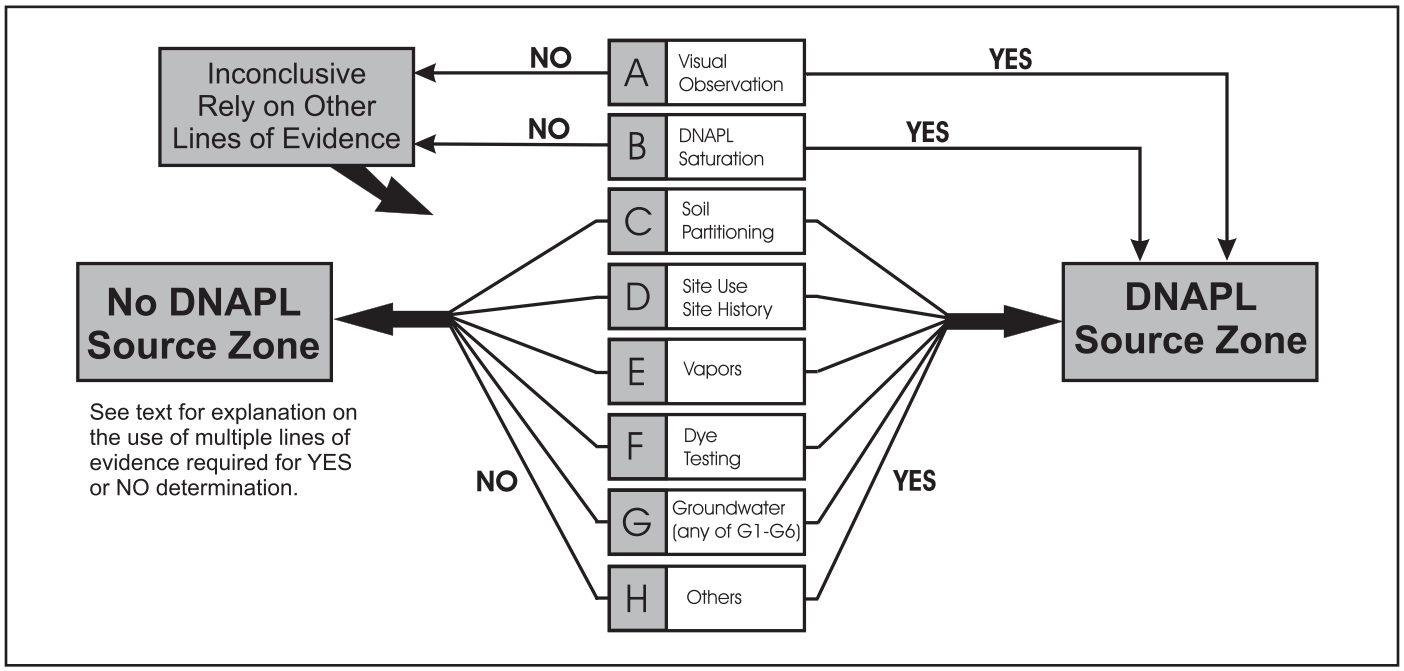

Figure 3 – Converging lines of evidence approach to assessing DNAPL presence. Methods B and C are not applicable to fractured rock.

combining to form either a positive or negative determination. Note that it is not likely that all of C through H will be satisfied at any one particular site, and that neither A nor B are necessary requirements to conclude that DNAPL is present. Most confirmed DNAPL source zones will have some of A through H determined to be negative. Because conditions vary from site to site, this document does not prescribe a specific number of lines of evidence that must be satisfied to arrive at either a positive or negative determination.

If the various lines of evidence contradict each other, it may be necessary to collect more data. It is possible that a minority of positive determinations can outweigh a majority of negative determinations if the positive lines of evidence cannot be explained without the presence of DNAPL. It should also be noted that not all sites lend themselves to collecting all of the types of data outlined here. In fractured rock, for example, soil vapor data and partitioning calculations would not be relied upon.

Evaluating the presence of DNAPL is an iterative process that incorporates new data as they are obtained. It is recognized here that certain types of data are more likely to be collected in the early stages of site investigation, while others (e.g., groundwater concentrations) can be collected on a routine basis throughout the investigation process. The fact that a number of lines of evidence are outlined in Figure 3 does not suggest that they should all be pursued at any one particular site. Site specific conditions will dictate what lines of evidence should be pursued. Care should be taken, however, to ensure that a negative response to the various lines of evidence is not simply attributable to inadequate characterization and an insufficient amount of data.

6.0 - Delineation of the DNAPL Source Zone

Depending on the spatial density of sampling points installed during initial investigation efforts, the general area within which the DNAPL resides may have been identified. Once it has been determined that DNAPL is present in the subsurface, the objectives for delineation of the source zone can be established. These objectives can vary from site to site, but typically involve one or more of the following:

- Delineation of the DNAPL source zone to ensure that the flow paths and quality of the groundwater downgradient of the source zone are monitored for the presence of dissolved-phase contaminants to assess protection of current and potential receptors.
- Delineation of the DNAPL source zone to facilitate proper design of containment systems involving groundwater extraction and/or physical barriers.
- Delineation of the DNAPL source zone to facilitate implementation of DNAPL mass removal technologies.
- Delineation of the DNAPL source zone as part of establishing boundaries for institutional controls.
- Delineation of the DNAPL source zone as part of Technical Impracticability assessments (41).

Given the selective nature of DNAPL migration, it is not feasible to determine the exact location and extent of individual DNAPL migration pathways within the overall confines of the source zone in either unconsolidated deposits, or fractured bedrock. Because data collection efforts typically involve a finite number of local-scale measurements taken at discrete locations (e.g., water quality samples, soil samples, etc.), some uncertainty will exist regarding the delineated spatial extent of the source zone.

To address the issue of uncertainty, it is recommended that both a 'Confirmed/Probable' DNAPL source zone be delineated, as well as a 'Potential' DNAPL source zone (see Figure 4). The Confirmed/Probable source zone is the volume within which compelling and multiple lines of evidence indicate that DNAPL is present. Note that what may be a compelling line of evidence at one site may not be so at another site (e.g., G2 Persistent Plume, is a stronger line of evidence in a high permeability setting than at a site where back-diffusion may dominate). The Potential source zone is of larger spatial extent, and is defined as that volume of the subsurface within which some lines of evidence indicate that DNAPL may be present, but the lines of evidence are not as numerous, consistent, or compelling as within the Confirmed/Probable source zone. Defining a Potential source zone outside of the Confirmed/Probable source zone addresses the uncertainty associated with finite amounts of data. This can be particularly useful in the hydraulically downgradient direction where it is often difficult to determine the distance to the edge of the DNAPL source zone based on groundwater quality data (e.g., using lines of evidence G1 through G6).

With respect to the various criteria for assessing DNAPL presence outlined in Section 4, lines of evidence A and B will both fall within the Confirmed/Probable source zone. All other lines of evidence (C through H) could fall within either the Confirmed/Probable source zone, or the Potential source zone. Note also that positive determinations for lines of evidence A and B are not necessary to define a Confirmed/Probable source zone. The defining feature of the Confirmed/Probable source zone is that multiple lines of evidence indicate that DNAPL is present. In practice, this will manifest itself as various lines of evidence all plotting within the same general spatial area on plan view and cross-section figures (see Figure 4 for plan view example). Within the Potential source zone, there will be fewer lines of evidence, and their occurrence may not be as contiguous as within the Confirmed/Probable source zone. Consideration should be given to known DNAPL release locations and structural aspects of the geology (e.g., dipping beds, dipping fractures) when delineating both the Confirmed/Probable and Potential source zones.

There is no prescriptive number of lines of evidence that separate the two source zone delineations. The individual lines of evidence cannot be weighted either, as the strength of the uncertainty/certainty determination is dependent on how often more than one line of evidence occurs at a particular location and how many contiguous locations have multiple lines of evidence; assigning a weighting factor to each line would negate this objectivity. Furthermore, many factors influence the transport of the DNAPL and the associated concentration of the dissolved-phase constituents such that a weighting factor could not be fairly assigned for all types of hydrogeologic environments and types of DNAPL contaminants.

The amount of acceptable uncertainty in delineating the source zone boundaries is likely to be dependent on the remedial actions considered. If hydraulic or physical containment of the DNAPL source zone were a component of the remedial actions, for example, an accurate delineation of the Potential source zone would be war-

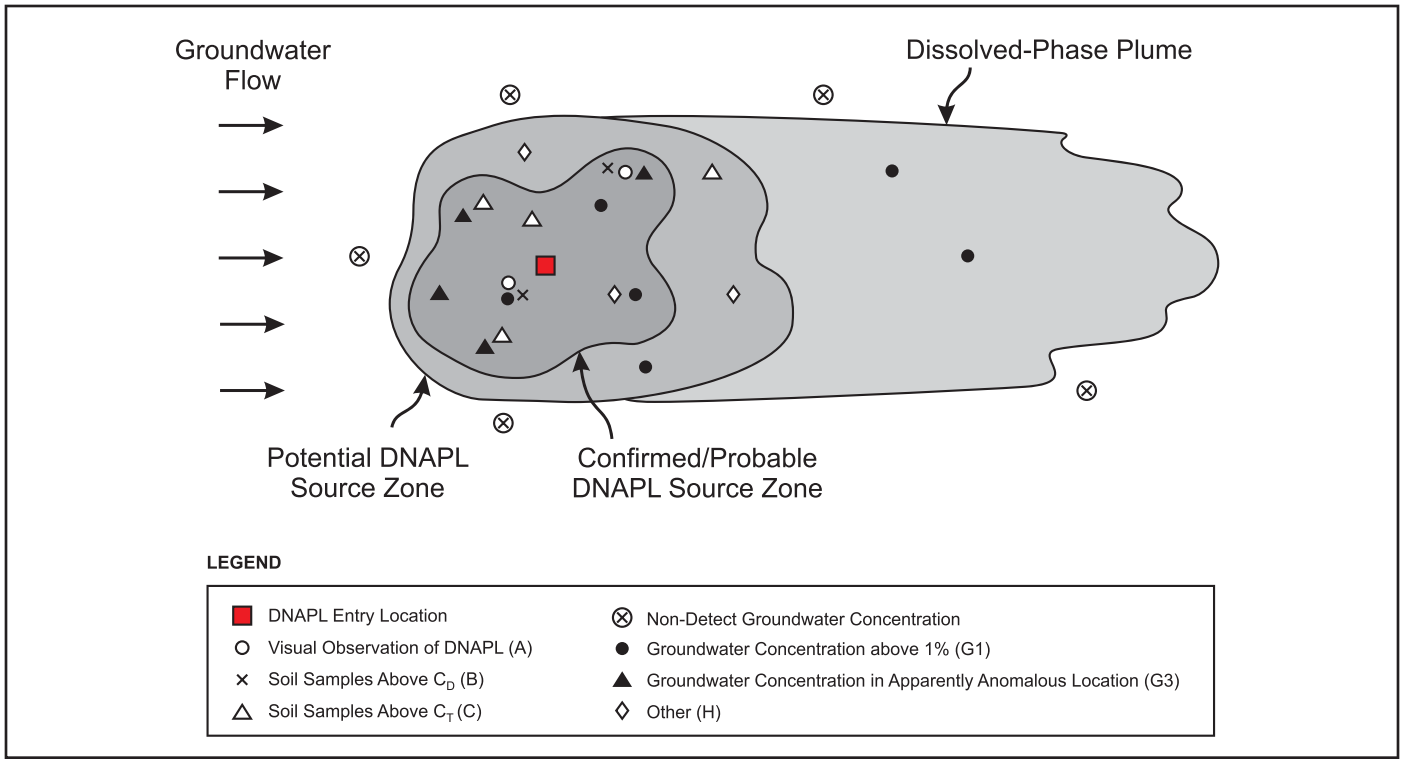

Figure 4 – Example of plan view schematic illustrating confirmed/probable and potential DNAPL source zones. Note that not all lines of evidence are depicted. Types and distribution of lines of evidence will vary from site to site.

ranted (the likely target for hydraulic containment) and accurate delineation of the Confirmed/Probable source zone may not be necessary. If the remedial actions included implementation of a DNAPL mass removal technology, however, then an accurate delineation of the Confirmed/Probable DNAPL source zone (the likely target for mass removal) would be warranted. A similar approach may be appropriate for designating a zone of technical impracticability (TI). Overestimating the size of the Confirmed/Probable source zone could overstate costs for technology application and may result in a particular technology being screened out. Underestimating the size of the Confirmed/Probable source zone, on the other hand, could lead to underestimation of costs and the perception of poor performance following completion of technology application. Monitoring points outside of an underestimated source zone may provide data showing little, if any, benefit resulting from source zone removal or treatment.

Typically, to refine the locations of the boundaries, additional drilling and sampling may be required between the Confirmed/Probable and Potential DNAPL areas. Figure 5 depicts an iterative process of data collection. Usually the degree of uncertainty in delineating these two zones will be greater in a more complex hydrogeologic environment. Although additional sampling points may be easily installed in shallow, unconsolidated materials, the same level of effort may not be feasible or may be cost prohibitive in deep fractured rock. Care must also be taken to ensure that drilling and sampling activities do not mobilize DNAPL deeper in to the subsurface. Strategies in place of extensive drilling to depth within the source zone include drilling adjacent to the suspected source zone and using lines of evidence such as G1 through G6 to infer DNAPL presence in the upgradient direction.

In all environments, the risks of potentially mobilizing the DNAPL and the associated incremental costs of additional sampling points should be compared to the benefits of increased ability to evaluate the spatial extent of the DNAPL. Additionally, site investigators should have a DNAPL Contingency Plan on hand in the field to address actions to be taken if pooled DNAPL is encountered during drilling. At some sites, it may be desirable to adopt an 'outside in' approach to reduce the number of invasive borings that need to be placed within the DNAPL source zone.

In addition to delineating the spatial extent of the source zone, investigators may need to assess whether or not DNAPL is still migrating within the subsurface. The assessment of mobility can be carried out using screening calculations (27) and observations such as an expanding area of lines of evidence indicating DNAPL presence. Other features of the source zone that may be of interest include the mass of DNAPL present, the mass flux downgradient of the source zone, and the relative proportions of residual versus pooled DNAPL. Calculation 1 can be used to distinguish between residual and pooled DNAPL in soil samples by selecting a saturated threshold above which DNAPL is considered pooled. Also of note is the fact that residual DNAPL will not enter monitoring wells, implying that the accumulation of DNAPL in a well indicates the presence of pooled DNAPL in the formation. Details regarding how to estimate the mass of DNAPL present in a source zone or the distribution of mass flux downgradient of the source zone, however, are beyond the scope of this document.

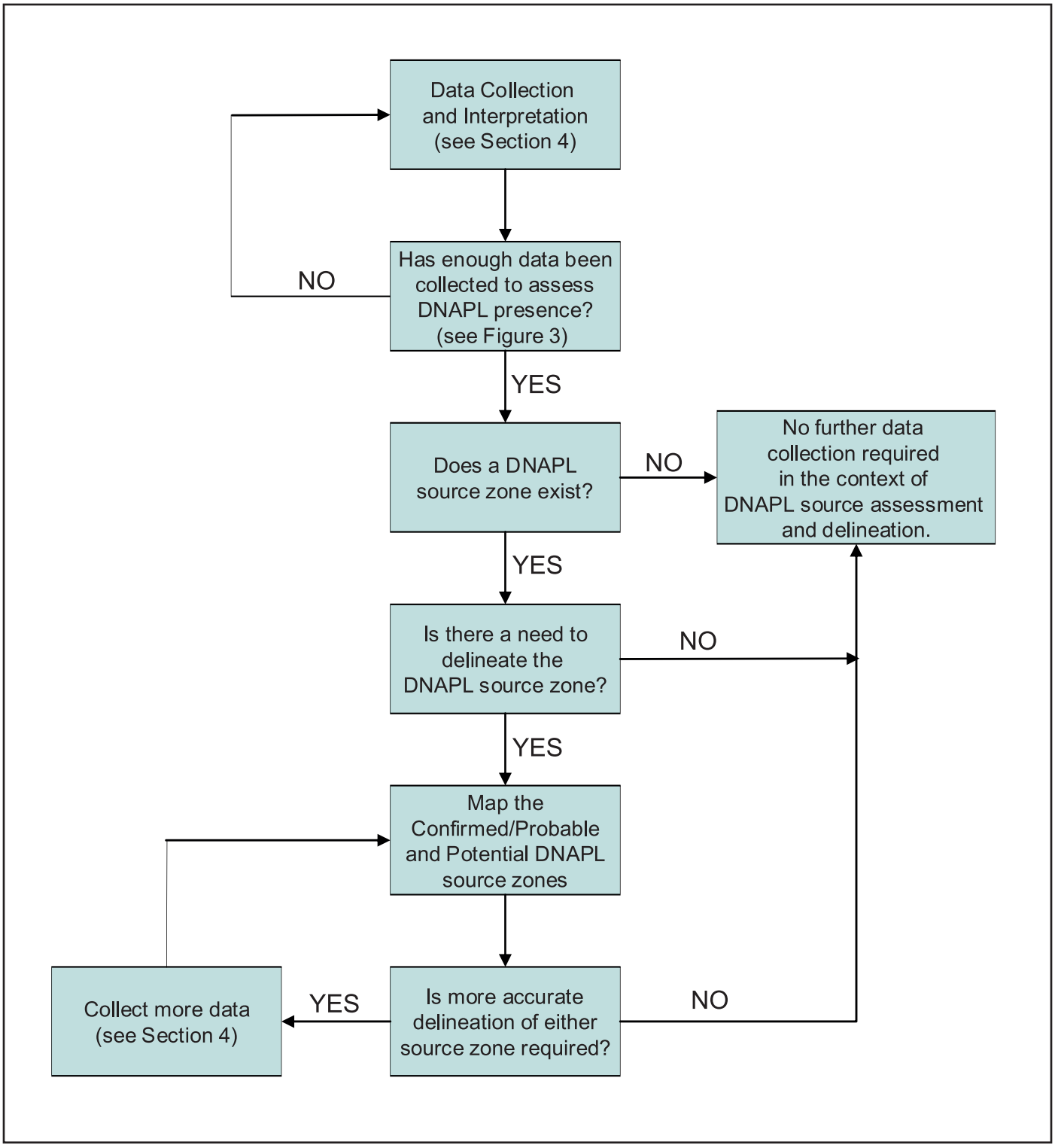

Figure 5 - Flowchart depicting iterative data collection process used in refining the DNAPL source zone boundaries.

7.0 - Glossary

Bulk Retention Capacity is defined as the total volume of DNAPL that has been retained as residual and pooled DNAPL in a unit volume of the subsurface. The bulk retention capacity accounts for the fact that not all lenses, laminations and geological units within a source zone contain DNAPL (27), and it is a function of the release history, geology and DNAPL properties. In unconsolidated media, the bulk retention capacity can be in the range from 0.005 to 0.03 (36). In fractured media, the bulk retention capacity can be in the range of 0.0002 to 0.002 (36). Fractured rock and clay cannot retain as much DNAPL per unit volume as unconsolidated deposits.

Capillary Barriers are fine grained lenses, layers and laminations upon which lateral spreading and pooling of DNAPL can occur. Even if the capillary barrier is penetrated by the DNAPL, it is likely that lateral spreading will have occurred along the top surface of the barrier prior to the capillary pressure having exceeded the entry pressure of the barrier. The finer grained the capillary barrier, the higher the pool height of DNAPL that it can support (17).

Capillary Pressure is the pressure difference between two immiscible liquids and arises because of interfacial tension. It is calculated as the non-wetting phase pressure minus the wetting phase pressure. If the DNAPL is the non-wetting phase and water is the wetting phase, for example, the capillary pressure would be the DNAPL pressure minus the water pressure.

DNAPL (Dense, Non-Aqueous Phase Liquid) is an organic liquid that is more dense than water and does not mix freely with water. A ***single-component DNAPL*** is composed of only one chemical. A ***multi-component DNAPL*** is composed of two or more chemical components.

DNAPL Source Zone The DNAPL source zone is the overall volume of the subsurface containing residual and/or pooled DNAPL. Not all portions (e.g., lenses, laminations, or fractures) of the source zone will contain residual and/or pooled DNAPL. The ***Confirmed/Probable DNAPL Source Zone*** is the part of the source zone within which it is known or highly likely that DNAPL exists. The ***Potential DNAPL Source Zone*** is the part of the source zone within which it is possible that DNAPL exists, but the lines of evidence indicating DNAPL presence are either fewer or are not as strong as those associated with the Confirmed/ Probable DNAPL Source Zone.

Dissolved-phase Plume The zone of contamination containing dissolved-phase constituents resulting from groundwater flowing past residual and pooled DNAPL. The contaminants present in the plume are subject to advection, dispersion, and possibly sorption, decay, and matrix diffusion. Dissolved-phase plumes can be sustained by back diffusion from low permeability regions in the absence of DNAPL.

Effective Solubility For a multi-component DNAPL, the equilibrium solubility in water of any component of the DNAPL is referred to as the component's effective solubility. In general, the various components of a DNAPL suppress each other's aqueous solubility implying that effective solubilities are typically less than single-component (handbook) solubilities. For structurally similar compounds, the effective solubility can be estimated using Raoult's Law (2).

Interfacial Tension (IFT) is a tensile force that exists in the interface separating DNAPL and water. Because of interfacial tension, DNAPLs do not mix freely with water and exist in the subsurface as a separate liquid phase. IFT is a site-specific value that can be assessed with a simple laboratory test if a sample of DNAPL can be obtained. Literature values tend to overestimate the IFT encountered at sites. In general, higher IFT leads to more lateral spreading of DNAPL in horizontally bedded deposits, stronger capillary trapping forces, and a greater tendency for DNAPL pooling.

Mole Fraction refers to the proportion of a component, on the basis of moles, in a multi-component DNAPL. The sum of all the mole fractions is unity. Mass fractions, as provided by laboratory analysis, can be converted to mole fractions using the molecular weight of each component (see calculation 5).

1% Rule of Thumb is a generality that sampled groundwater concentrations in excess of 1% effective solubility (see Calculation 3) indicate that DNAPL may be present in the vicinity of (any direction) the monitoring point of interest. The distance between the monitoring point in question and the DNAPL source zone varies from site to site and is generally difficult to quantify with a high degree of accuracy.

Pooled DNAPL refers to local, continuous distributions of DNAPL that accumulate above capillary barriers. The capillary barriers are typically lower permeability horizons, and they can occur at any elevation in the subsurface. Within the pool, the DNAPL saturation is typically between 30% and 80% of pore space in both porous media and fractures (27). Because pools are contiguous through the pore structure they are potentially mobile and can migrate into monitoring wells, and can be mobilized by increases in the hydraulic gradient or lowering of IFT.

Raoult's Law is given by $C_i = m_i S_i$ where C_i is the effective solubility (mg/l) of component *i*, m_i is the mole fraction (unitless) of component *i* in the DNAPL, and S_i is the single-component (handbook) solubility of component *i* (2). This expression assumes ideal partitioning behavior and is used to estimate the maximum concentrations in groundwater immediately adjacent to residual and pooled DNAPL.

Residual DNAPL refers to disconnected blobs and ganglia of the DNAPL, trapped by capillary forces in the pore space of both porous media and fractures (21, 27, 44). The blobs and ganglia are typically from 1 to 10 grain diameters in size in unconsolidated deposits (44), and are left behind in the pathways that DNAPL has migrated through.

Residual Saturation refers to the volume of residual DNAPL present in a unit volume of pore space. Residual DNAPL saturations typically vary between 5% and 30% of pore space in both porous media and fractures (21, 27, 44).

Source Zone Architecture refers to (i) the overall shape and dimensions of the source zone, (ii) the ratio of residual to pooled DNAPL (also referred to as the ganglia to pool ratio), (iii) the lateral continuity of zones of residual DNAPL and DNAPL pools, (iv) the thickness of zones of residual DNAPL and DNAPL pools, and (v) the portion of lenses and layers containing DNAPL versus those void of DNAPL. The source zone architecture influences the downgradient dissolved-phase plume concentrations and mass flux distribution.

Wettability refers to the affinity of the DNAPL for a solid surface in the presence of water (6, 27). Many DNAPLs are non-wetting, implying that they will preferentially occupy the pore spaces within coarser grained lenses and laminations, and larger aperture fractures. Some DNAPLs are wetting with respect to water, however, implying that they will preferentially coat the aquifer materials and thereby occupy the pore spaces of the finer grained media. Coarser grained horizons and larger aperture fractures represent capillary barriers to DNAPLs that are wetting with respect to water.

Acknowledgements

The U.S. EPA Office of Research and Development (ORD) wishes to express their appreciation to the U.S. EPA Ground Water Forum. The Ground Water Forum was helpful in the development and review of this document along with ORD scientist Dr. David Burden.

Notice

The U.S. Environmental Protection Agency through its Office of Research and Development and the Office of Superfund Remediation and Technology Innovation funded and collaborated on the document under Contract No. 68-C-02-092 to Dynamac Corporation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Appendix A - Example Calculations

Note that the following calculations are generally subject to uncertainty because of input parameter variability. This variability may stem from spatial or temporal variation in site-specific conditions, or variation in textbook parameters such as contaminant chemical properties. The investigator is advised to make conservative choices with respect to input parameters and consider using a range of either measured or estimated values when performing calculations.

Calculation 1 – Chemical Concentration in Soil Corresponding to Threshold DNAPL Saturation

$$C_D = \frac{S_r \phi \rho_N 10^6}{\rho_b} + C^T$$

- C_D = soil concentration (mg/kg) corresponding to threshold DNAPL saturation [calculated],
- S_r = threshold DNAPL saturation [set between 0.05 and 0.10],
- ϕ = effective porosity (unitless) [site specific measurement],
- ρ_N = DNAPL density (g/cc) [site specific measurement],
- ρ_b = dry soil bulk density (g/cc) [site specific measurement],
- C^T = amount of contaminant (mg/kg) present in the soil sample in the aqueous, vapor, and sorbed phases [see Calculation 2 to evaluate C^T].

Example Calculation

PCE DNAPL (ρ_N = 1.62 g/cc) in a soil sample with S_r = 0.05, ϕ = 0.25 and ρ_b = 2.0 g/cc corresponds to (ignoring the C^T fraction) C_D = 10,125 mg/kg. Note that the quantity C^T is typically negligible compared to the DNAPL saturation term. The above equation is applicable to single-component DNAPLs in unconsolidated porous media. See reference (25) for the relationship between C_D and DNAPL saturation for a multi-component DNAPL. It should be noted that $0.05 \leq S_r \leq 0.10$ is suitable for geologic deposits having typical ranges of f_{oc} values (i.e., less than 2%). In general, the value of S_r should be chosen such that the resulting C_D is at least an order of magnitude higher than the C^T in calculation 2 arrived at using the highest f_{oc} value measured at the site.

Calculation 2 – Threshold Chemical Concentration in Soil Based on Partitioning Relationships (see Ref. 11)

$$C_i^T = \frac{C_i}{\rho_b}\left(K_d \rho_b + \theta_w + H'\theta_a\right)$$

- C_i^T = soil concentration (mg/kg) threshold for component *i* [calculated],
- C_i = effective solubility (mg/l) [see Calculation 3] of component *i* [calculated],
- ρ_b = dry soil bulk density (g/cc) [site specific measurement],
- K_d = soil-water partition coefficient (ml/g) [calculated using $K_d = K_{oc} f_{oc}$],
- θ_w = water-filled porosity (unitless) [calculated from site specific measurement of moisture content],
- H' = unitless Henry's constant [handbook],
- θ_a = air-filled porosity (unitless) [site specific measurement],
- K_{oc} = organic carbon - water partition coefficient (ml/g),
- f_{oc} = fraction organic carbon (unitless) [site specific measurement].

C_i^T represents the maximum amount of contaminant *i* that can be present in a porous media sample in the sorbed, aqueous, and vapor phases without a DNAPL phase present. The calculation can be applied below the water table by setting $\theta_a = 0$. Note that the water-filled porosity and the air-filled porosity sum to the total porosity. Note also that the calculation of C_i^T is typically more sensitive to f_{oc} than it is to the porosity values.

Example Calculation

Consider a single-component DNAPL composed of TCE (C_i = 1100 mg/l, K_{oc} = 126 ml/g, H' = 0.31) in a soil sample having θ_w = 0.15, θ_a = 0.10, ρ_b = 2.0 g/cc, and f_{oc} = 0.003. The corresponding value of C^T is 515 mg/kg. For a multi-component DNAPL, a separate value of C_i^T would be calculated using the above equation for each component detected in the soil sample.

Calculation 3 – Effective Solubility Calculated Using Raoult's Law (see Ref. 2)

$$C_i = m_i S_i$$

- C_i = effective solubility (mg/l) of component *i* [calculated],
- m_i = mole fraction (unitless) of component *i* in the DNAPL [site specific measurement],
- S_i = single-component solubility (mg/l) of component *i* [handbook].

Example Calculation

Consider a 3-component DNAPL composed (by mass) of 25% TCE (S_i = 1100 mg/l), 35% PCE (S_i = 200 mg/l), and 40% toluene (S_i = 500 mg/l); the corresponding mole fractions (see Calculation 5) are 0.23, 0.25, and 0.52 respectively, and the corresponding effective solubilities are 250 mg/l, 50 mg/l, and 260 mg/l respectively. Sampled groundwater concentrations in excess of 1% of any of these effective solubilities are evidence of possible DNAPL presence in the vicinity of the monitoring point. The distance to the DNAPL cannot be determined on the basis of the magnitude of the groundwater concentration alone. In cases where some of the components of the DNAPL are not known, the unknown mass fraction can be assigned an estimated molecular weight, or the average of the molecular weights of the known components.

Calculation 4 – Threshold Chemical Concentration in Soil Based on Partitioning Relationships Where Composition of DNAPL is Not Known

$$\sum_{i=1}^{n} \frac{C_{obs,\,i}^T}{C_{S,\,i}^T} \geq 1$$

- $C_{obs,\,i}^T$ = reported concentration (mg/kg) of component *i* [site specific measurement],
- $C_{S,\,i}^T$ = single component soil partitioning concentration (mg/kg) of component *i* (see C_i^T in Calculation 2),
- n = number of components observed in the soil sample [site specific measurement].

For a multi-component DNAPL of unknown composition, the sum of the mole fractions must equal unity. DNAPL will therefore be present in a soil sample if sum of $\frac{C_{obs,i}^T}{C_{S,i}^T}$ exceeds unity.

Note that $C_{S,\,i}^T$ is calculated for each component in the summation using Calculation 2 with the single-component solubility as input. The presented technique can be prone to false negatives in cases where the soil sample was not analyzed for some of the components of the DNAPL. Because of this, it may be prudent in some cases to only use the calculation for demonstrating that DNAPL was present in a soil sample and not rely upon it to demonstrate that DNAPL was absent from a soil sample.

Example Calculation

The table below provides an example calculation for a soil sample in which 5 components have been detected. The sample is characterized by a porosity of 25%, a fraction organic carbon of 0.003, and a dry bulk density of 1.99 g/cc. The last column of the table sums to greater than 1.0, indicating that DNAPL was present in the soil sample.

Compound	$C^{T}_{obs,\,i}$ *(mg/kg)*	K_{OC} *(l/kg)*	*Handbook Solubility (mg/l)*	$C^{T}_{S,\,i}$ *(mg/kg)*	$\frac{C^{T}_{obs,i}}{C^{T}_{S,i}}$
Trichloroethylene	145	126	1100	554	0.262
Tetrachloroethylene	155	364	200	244	0.636
Carbon Tetrachloride	200	439	790	1140	0.175
Chlorobenzene	177	330	500	558	0.317
1,1,1-Trichloroethane	213	152	1320	768	0.277
				SUM =	**1.668**

Calculation 5 – Mole Fraction (n-component DNAPL)

$$m_i = \frac{\frac{ms_i}{mw_i}}{\frac{ms_i}{mw_i} + \frac{ms_{i+1}}{mw_{i+1}} + \ldots \frac{ms_n}{mw_n}}$$

m_i = mole fraction of component *i* (unitless) in the DNAPL [calculated],

ms_i = mass fraction of component *i* (unitless) in the DNAPL [measured],

mw_i = molecular weight (g/mol) of component *i* [handbook].

Example Calculation

Consider a 3-component DNAPL composed by mass of 25% TCE (*mw* = 131.5 g/mol), 35% PCE (*mw* = 165.8 g/mol), and 40% toluene (*mw* = 92.1 g/mol). The corresponding mole fractions are 0.23, 0.25, and 0.52 respectively. In cases where some of the components of the DNAPL are not known, the unknown mass fraction can be assigned an estimated molecular weight, or the average of the molecular weights of the known components.

Calculation 6 – 1% Effective Solubility Threshold Not Knowing DNAPL Composition

$$\sum_{i=1}^{n} \frac{C_i^{obs}}{S_i} = \alpha$$

C_i^{obs} = sampled groundwater concentration (mg/l) of component *i* [site specific measurement],

S_i = single-component solubility (mg/l) of component *i* [handbook],

α = cumulative mole fraction of the sample [set],

n = number of components in groundwater sample.

Calculation assumes that the degree of borehole dilution, dispersion, and degradation is identical for each component of interest in an obtained groundwater sample. If the 1% rule-of-thumb is used, DNAPL may be present in the vicinity of a monitoring well if $\alpha > 0.01$. The procedure can be applied on a sample-by-sample basis without having to make the assumption that the DNAPL composition is spatially uniform in the subsurface. If it is believed that a value other than 1% effective solubility indicates DNAPL presence, α can be set to the corresponding value. The presented technique can be prone to false negatives where the groundwater sample was not analyzed for some of the components of the DNAPL. Because of this, it may be prudent in some cases to only use the calculation for demonstrating that α has been exceeded in a sample and not rely upon it to demonstrate that α was not exceeded in a sample.

Example Calculation

The table below presents an example calculation for 5 components. Although each component has been detected at a concentration less than 1% of S_i, the cumulative mole fractions sum to 3.4%, providing evidence of possible DNAPL presence in the vicinity of the monitoring location. If the groundwater sample is not analyzed for all components present in the DNAPL, or if any compounds are degrading in the aqueous phase, the calculation procedure will underestimate the likelihood of DNAPL presence.

Compound	C_i^{obs} ***(mg/l)***	S_i ***(mg/l)***	$\frac{C_i}{S_i}$
Trichloroethene	4.4	1100	0.004
Tetrachloroethene	1.8	200	0.009
Toluene	3.5	500	0.007
Chlorobenzene	4.0	500	0.008
Trichloromethane	48.0	8000	0.006
$\sum \frac{C_i^{obs}}{S_i}$			**0.034**

Calculation 7 – Plume Detachment Time

$$t = \frac{LR}{v}$$

- t = time (yrs) required for contaminants to migrate through source zone of length L in the direction of groundwater flow,
- v = average linear groundwater velocity (m/yr) [site specific],
- R = retardation factor (unitless) for the contaminant of interest [site specific measurement – see calculation below],
- L = length (m) of source zone in direction of flow [site specific measurement].

Calculation assumes unidirectional, steady-state flow conditions subject to advection and sorption only (dispersion and matrix diffusion are ignored). The calculation assumes that contaminant mass is not being added to the saturated flow system from any unsaturated zone sources (e.g., leaching and desorption). Note that R is often approximated in unconsolidated media by

$$R = 1 + \frac{\rho_b}{\phi} K_{oc} f_{oc}$$

where ρ_b is the dry bulk density (g/cc), ϕ is the porosity (unitless), K_{oc} is the organic-carbon partition coefficient (ml/g), and f_{oc} is the fraction organic carbon (unitless). Calculations considering dispersion and degradation can be found in (10).

Example Calculation

Using L = 50 m, v = 25 m/yr, and R = 5, the source zone should be flushed of dissolved and sorbed contaminants in approximately 10 years following the last release of contaminants. Dispersion, which always occurs, will lengthen this time as will back-diffusion, if it is occurring. In cases where complicated flow conditions exist and where it is desired to account for dispersion and back-diffusion, numerical models can be used to perform the assessment.

Calculation 8 – Conversion to Parent Compound

Daughter product concentrations can be converted to equivalent parent product concentrations by converting the daughter mass/volume concentrations to moles/volume, attributing that number of moles to the parent, and then converting the parent concentration to mass/volume.

Example Calculation

Consider a groundwater sample containing 500 ppb PCE, 400 ppb TCE, 1300 ppb cis-1,2 DCE and 44 ppb VC at a site where it is known that only PCE was released to the subsurface. It is assumed that biodegradation has not progressed beyond VC. The PCE concentration of 500 ppb is less than 1% of the PCE solubility (1% PCE solubility is 2000 ppb). Given TCE, cis-1,2 DCE and VC molecular weights of 131.5, 97.0 and 62.5 g/mol, respectively, the groundwater concentrations of these compounds are equal to 3.042E-06 mol/l, 1.340E-05 mol/l and 7.040E-07 mol/l, respectively. Assuming that each mole of daughter product derives from one mole of parent product, the equivalent total concentration of parent product is 2.016E-05 mol/l. This corresponds to an equivalent parent (PCE) concentration of 3343 ppb (PCE molecular weight 165.8 g/mol), which exceeds the 1% solubility value of 2000 ppb.

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September 2009

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