

Dense non-aqueous phase liquids: Site remediation and redevelopment

Site characterization methods and benefits

Purpose

This document provides guidance on the processes used to characterize sites with dense non-aqueous phase liquid (DNAPL). It also provides a background on why proper DNAPL site characterization is important at the beginning of a site investigation. In addition, this guidance also includes a discussion of the benefits of proper characterization, methods and tools that can be used, and a sampling guidelines section for site investigation.

While this document specifically addresses DNAPL characterization, the characterization processes and tools presented may be applicable to other site situations such as with petroleum hydrocarbons and metals. Please consult the MPCA project team to determine the applicability for your particular site situation.

What is Integrated Site Characterization (ISC)?

ISC is an iterative process that utilizes all available site information including site history, geology, hydrogeology and chemistry to help define the conceptual site model (CSM) and how this information inter-relates. Additional information is discussed in [ITRC, 2015](#). The end goal of characterization is to develop a competent CSM that provides the foundation for all subsequent decisions. A quality CSM relies on high-resolution site characterization (HRSC) to develop a detailed understanding of the four pillars of site characterization:

- Site history-types of chemicals use and quantities, chemical location/storage, disposal/handling practices;
- Geology- lithology, structure, anisotropy and heterogeneity;
- Hydrogeology- matrix flow and fracture characteristics; and
- Chemistry- diffusion, dispersion, solubility, degradation, chemical partitioning;

The 14-Compartment Model process described on the CSM Development guidance should be used to assist with the characterization and the development of the CSM.

Key concepts for implementing ISC

- **Heterogeneity replaces homogeneity** – Subsurface geology is not homogenous; both micro- and macro-scale geology differences play a substantial role in the fate and transport of DNAPL.
- **Anisotropy replaces isotropy**- The subsurface is not uniform in all directions; subsurface properties vary with direction (geologic anisotropy). This anisotropy plays a substantial role in the fate and transport of DNAPL.
- **Diffusion replaces dispersion**- Matrix diffusion largely controls lateral and vertical contaminant distribution in the subsurface.
- **Back-diffusion is a significant source of contamination and plume growth**- High contaminant concentrations in a high-permeability media diffuse into lower-permeability media. The lower-permeability media acts as a “secondary source” once the concentrations in the higher-permeability media have been reduced (due to remediation or natural attenuation).

- **Non-Gaussian distribution replaces Gaussian distribution-** Statistical methods that assume geology is normal (Gaussian) are not effective for characterization because of how geology is typically deposited. The actual distribution of permeable units is best represented by a lognormal or (less commonly) a nonparametric distribution.
- **Transient replaces steady state conditions-** Site conditions may appear to be steady state, but equilibrium is dynamic. Conditions change due to a number of factors (ex: how plume migrates, how it degrades, how source material is depleted, geologic interaction by migrating contaminants, etc.). In the absence of data to support it, steady state conditions should not be assumed.
- **Nonideal replaces ideal sorption-** Ideal sorption behavior indicates the forward reaction (adsorption) and reverse reaction (desorption) are reversible, providing identical isotherms at equilibrium. However, aging or prolonged soil-contaminant exposures can result in situations where it is difficult to remove contaminants from the solid phase (nonideal behavior). This can result in a continued release to the impacted aquifer. The nonideal behavior can be confused with either nonlinear desorption or rate-limited mass transfer. Do not assume ideal sorption behavior in the absence of data to support it.

What methods should I use?

Characterization methods should be selected based on the data collection objectives. Is the objective to collect geology data? hydrogeology data? chemistry data? Consider too, that data quality (quantitative vs. qualitative data) affects method/tool selection. One method is HRSC, which is discussed below. Note: HRSC may include the following:

- High frequency sampling,
- Downhole testing (video log),
- Visual indication of soil samples,
- Tracers (Partitioning Inter-well Tracer Test),
- Sorption (NAPL flexible liner underground technologies),
- Laser induced fluorescence (LIF),
- Dye testing,
- Colorimetric screening,
- Conductivity (interface probes),
- Passive and active soil gas surveys,
- Hydraulic profiling tools, and
- Laboratory analysis (fixed, mobile, portable gas chromatograph, portable gas chromatograph/mass spectrometer).

Other methods may be more appropriate and can be found on the [ITRC tool selection worksheet](#) (discussed below). Note that the worksheet can be used to select a tool based on the data collection objectives.

What is High Resolution Site Characterization and why should it be used?

Conventional methods are executed at a precision of meters that infers the extent of contaminant storage areas and transport between sample locations. Typically, the traditional investigation locations are based on site history, Darcy flux, site observations, etc. This does not account for variability in the subsurface that is identified through HRSC methods which are executed at a precision of centimeters. HRSC techniques collect a high density of samples and measurements at an appropriate scale to identify contaminant distribution and small-scale heterogeneities where significant contaminant transport and storage may occur (see DNAPL Properties guidance).

Additional information on HRSC can be obtained [via CLU-IN](#).

High Resolution Site Characterization also provides for:

- Proper identification of permeable and transmissive zones including small scale features such as fractures and thin bed changes in texture and facies (high permeability zones act as contaminant transport zones and low-permeability zones retain and slowly release contaminants);
- Improved accuracy of the conceptual site model (CSM) and better knowledge of contaminant distribution;
- A reduction in uncertainty for risk evaluation, remedy selection, and site management decisions;
- Identification of better performing remedies as well as having better predictability of plume behavior/risks; and
- HRSC reduces the total project life cycle costs and allows for an improved return on investigation.

Tool Selection Worksheet

The [ITRC Integrated Site Characterization document \(ITRC, 2015\)](#) includes a [Tool Selection Worksheet](#) that can be used as part of the characterization. The document also includes a description of limitations and advantages for each of these methods. However, some technologies that may be appropriate for petroleum investigations, like bag headspace with a photoionization detector (PID), may not be suitable for DNAPL characterization. Some example scenarios are presented below.

Scenario*	If...	Then consider using one (or more) of the following...
1	Looking for the presence of DNAPL in a bedrock aquifer	GPR, PITT, discrete sampling (liner technology), microbial diagnostics.
2	Looking for contaminant concentration in unconsolidated deposits in the unsaturated zone	Induction resistivity, GPR Cross-Well Tomography, active soil gas surveys, portable gas chromatograph/mass spectrometry, ion trap mass spectrometry, MIP, colorimetric screening.
3	Looking for permeable units in unconsolidated material in the saturated zone	Nuclear magnetic resonance logging, packer testing, liner profiling, borehole dilution, flow metering, pumping/recovery tests, slug tests, constant head step test, tracer testing, hydraulic tomography, % recovery/RQD, physical properties, hydraulic profiling tool, EC.
4	Assessing porosity in unconsolidated material in the unsaturated zone	GPR, ERT, induction resistivity, GPR Cross-well tomography, optical televiewer, nuclear magnetic resonance logging, video log, core logging, physical properties.

*Use the ITRC tool selection worksheet to identify appropriate site-specific investigative tools

Site characterization steps

The goal of ISC is to continuously evaluate and update the CSM regardless of the site stage using multiple lines of inquiry.

[Appendix B of ITRC, 2015](#) presents case examples of ISC. [Chapter 4 of ITRC, 2015](#) presents the steps involved with a DNAPL site characterization, which generally include the following:

1. Define the problem and uncertainties and assess the conceptual site model using a model such as the 14-Compartment Model (CSM Development guidance). Determine if the CSM provides enough information and clarity to accurately assess risk and develop an appropriate remediation strategy.
2. Identify data needs/gaps and data resolution. Note specific data needs and the appropriate resolution to delineate subsurface heterogeneities that influence contaminant transport and distribution.
3. Establish specific data collection objectives. Table 4-1 of ITRC, 2015 provides examples of effective data collection objectives.
4. Design the process for data collection and analysis. Identify which investigative tools to use and how to analyze the data. The key objective is to collect data at sufficient frequency to meet the data collection

objectives, so there is no “one size fits all” approach. However, the Tool Selection Worksheet (ITRC, 2015) can be used to determine the best approach. Note that interpreting low concentrations of contaminants in high permeability zones while elevated concentrations of contamination are present in low permeability zones as “drilling out of contamination” may be misguided and should be a consideration as part of the data collection process.

5. Implement the investigation. Once the appropriate tools are selected, perform the investigation, and collect the data. Some investigation guidelines are provided in the next section.
6. Perform data evaluation and interpretation based on multiple lines of evidence. Evaluate the data obtained in the context of the conceptual site model (and how it pertains to all the data types) to make an informed remedial decision considering the geology, hydrogeology, and chemistry.
7. Update the conceptual site model and determine if objective(s) are met. Take the information obtained during the data evaluation/interpretation phase and determine if there are any additional data gaps or uncertainties in the 14-Compartment CSM prohibiting site environmental management. Revisit each step as necessary to obtain a sufficiently detailed conceptual site model. Note that the focus of the conceptual site model may shift from characterization toward remedy evaluation/selection as data is obtained.

Consider the following guidelines for characterization

Inadequate site characterization (e.g., attempting to characterize by “traditional” methods, not fully characterizing site geology, improperly characterizing the behavior and distribution of contaminants, etc.) results in having an incomplete conceptual site model. An incomplete CSM will result in more uncertainty and can lead to developing solutions that are not cost-effective to manage contaminated sites.

[Section 1.3 \(and figure 1.1\) of ITRC, 2015](#) presents the rationale for targeting project dollars towards proper investigation. Initially spending funds on a proper characterization result in a more accurate CSM from which an effective remedy can be developed. In this scenario, less funds are spent overall. Conversely, a minimally characterized site, while initially costing less, has an incomplete CSM. An ineffective remedy is developed from this incomplete CSM, which ultimately leads to more funds spent overall due to an incomplete understanding of the site.

In order to develop a CSM that effectively supports environmental management decision-making, be sure to follow the strategies outlined below:

- Boring logs should be completed, in detail, by a qualified geologist. The logs should include gradational changes, uniformity, primary components, secondary descriptions, minor percent of other particle sizes, structures (e.g., fractures), etc. Use the best combination of methodologies such as ASTM, USCS, and [EPA Environmental Sequence Stratigraphy \(ESS\)](#).
- Use an integrated method for managing uncertainty (such as the Triad approach, see the Triad resource website) at all sites. The Triad approach is comprised of three BMPs:
 - Systematic planning,
 - Dynamic work strategies (DWS) that efficiently address project concerns using real-time information, and
 - Use real-time measurement technologies that provide information in a timeframe sufficient to drive DWS.
- Provide a history of operations and all information to MPCA project staff including information related to chemical storage areas, disposal practices (pre and post RCRA) and accidental releases to direct characterization efforts in source or suspected source areas.
- Consider the composition of the chemicals purchased and how they were used to determine DNAPL composition. These are important because manufacturing processes change over time and knowledge of the chemical composition manufactured during a certain period can help explain the presence or

absence of degradation products in the dissolved phase plume. Also, used solvent mixtures may have different properties than virgin solvent.

- Consider when the release occurred, as the date can help in determining fate and transport related issues (ex: release points, liability, discrete/mixed plumes, natural attenuation, etc.)
- Evaluate all preferential pathways including natural pathways (e.g., thin sand lenses, variations in sand texture and composition, fracture openings, etc.) and man-made pathways (ex: utility lines/conduits, drainage systems, historic fill, etc.). This is important because DNAPL follows the “path of least resistance”, and these transport pathways can be used for enhanced DNAPL extraction during the remedial action.
- Focus characterization efforts on identifying areas where mass discharge is occurring because established research (Gilbeault, et. al 2005) concludes that 75% of contaminant mass discharge occurs in only 5-10% of the release cross sectional area.
- Define the extent of source area(s) in all directions and depths at a sufficient resolution to create and revise the CSM. Vertical and horizontal spacing is site-specific; however semi-quantitative methods (e.g., passive soil-gas) can be used as an initial “screening” method to identify focused areas where analytical samples may be collected.
- Conduct multiple high resolution transects in the down and cross-gradient direction of contaminant migration once source area(s) are identified. Transect spacing and depth is site dependent and should be conducted in a manner to fully delineate areas of mass discharge. When the plume cross sectional area and source area(s) are defined at sufficient resolution, a coarse sampling approach can be used to quickly delineate the plume periphery.
- Characterize low-permeability zones and their effect of mass diffusion in the low permeability zone or layer as these zones may be an ongoing source of contamination. Rather than limiting soil samples to specific thicknesses, focus the soil sample collection on intervals where a low-permeable zone is or may be present. Low permeability layers may consist of fine-grained sand, silt, clay, or any mixture containing these types of deposits. Field methods used to log borings (noted above) can be used to identify these zones.
- Select appropriate soil sampling methodology(ies) to use based on the information that is to be obtained. For example, DNAPL can easily be missed by collecting discrete samples from continuous soil cores. Consider using a MIP to identify areas for soil sample collection.
- Collect and analyze samples at a high frequency throughout the borehole. This is important because DNAPL concentrations can vary significantly over relatively small intervals.
- Collect media-specific (soil, groundwater, vapor) analytical samples at sufficient depth intervals to properly characterize saturated and unsaturated zones. Screening methods can be used to guide where to collect quantitative, media-specific, samples to meet investigation objectives. Analytical data is necessary to quantify contaminant mass, which is part of determining an appropriate remedial action.
- Take measures to ensure the vertical extent (soil, groundwater, and vapor) is properly characterized. Note that shallow excavations will not necessarily remediate a property because solvents will often easily go beneath the excavation depth.
- When using wells for the purposes of monitoring a plume, limit screen length to the impacted interval and note that screen length should not exceed 5 feet. Note that this does not apply to monitoring wells advanced solely for determining water table elevations as these wells serve a different function.
- As discussed in DNAPL Properties, DNAPL is mobile when it is continuous and its capillary pressure is high enough to exceed groundwater pore entry pressure, displace groundwater and migrate through the subsurface. DNAPL is considered immobile when DNAPL ganglia (discontinuous droplets) present in soil pore spaces cannot exceed the capillary pressure and displace groundwater in the formation. DNAPL is

potentially mobile if the DNAPL body is continuous, but its capillary pressure is not high enough to exceed groundwater pore pressure (ITRC 2015). If there is a concern that DNAPL is continuous and may become mobilized during drilling activities, additional site characterization may proceed if proper precautions are taken to avoid mobilization. These precautions include, but are not limited to:

- Utilize an appropriate drilling technology that seals off the sides of the hole with multiple casings during sample collection (e.g., sonic drilling, Direct push using Dual Tube[®] sampler).
- Use a step-down protocol using multiple telescoped isolation casings to determine the vertical extent of contamination. Collect samples from frequent intervals and test the samples for the presence of DNAPL before proceeding to the next interval.
- Utilize direct sensing tools e.g., DyeLIF[™] that do not require maintaining an open, uncased hole and provide real time data.
- Seal the borehole immediately upon completion of sample collection activities and before the outer casing is retracted.
- In cases where mobile DNAPL has been observed, utilize angle drilling or directional drilling techniques to place borings just outside the area of the identified mobile DNAPL.
- Certain types of well seals may be incompatible with the site-specific DNAPL. For example, creosote or TCE may create cracks in bentonite clay and create a pathway for vertical migration. Avoid drilling directly through mobile or potentially mobile DNAPL (i.e., an early-stage release) when possible, and always follow Minnesota Department of Health (MDH) well code. Consult with the MDH for grout performance if mobile or potentially mobile DNAPL is accidentally encountered, and the drilling activities breach a confining layer.
- Clay and shale layers have conventionally been considered barriers to DNAPL migration. However, in addition to diffusive transport, recent studies have demonstrated that chlorinated DNAPL waste can change the lattice structure of some water saturated clays and produce cracks which could play a significant role in the transport of chlorinated solvents (SERDP Project ER-1737, 2015). Since chlorinated DNAPL may significantly alter the structural integrity of some clay and shale layers, it should not be assumed that these layers will effectively limit chlorinated DNAPL transport in all cases. Vertical characterization of middle to late stage chlorinated DNAPL releases should extend past contaminated low permeability materials and potentially to underlying, subsequent layers of low permeability material until non contaminated low permeability layers can be documented.
- Use higher resolution methods to answer key components of the site conceptual model that remain unanswered after using conventional methods.
- DNAPL can move counter to groundwater flow, and this movement can extend contamination source areas that create unexpected areas of dissolved phase contamination. When monitoring at assumed downgradient locations (usually to delineate the upgradient presence of source zones and/or the extent of dissolved contamination), collect additional samples in assumed upgradient directions. This is needed to provide more certainty regarding the spatial distribution of the source zone.
- One technology is rarely sufficient to identify where to collect a lab sample (e.g., hydrophobic dyes and other visual sample examination techniques may fail to indicate the presence of DNAPL if the ratio of non-DNAPL soil to DNAPL is too high for easy detection). Instead of using a single technology (i.e., only visual sample examination techniques, or only hydrophobic dyes), use a multiple lines of evidence approach. Use the Tool Selection Worksheet to identify a series of tools to support this approach.
- Although PCE, with an ionization potential of 9.32eV (NIOSH, 1994), is detectable in vapor phase using a PID equipped with a 10.2 or greater eV energy source, do not rely on the bag headspace screening technique to field screen for characterization of chlorinated solvents to be analyzed in the laboratory for the following reasons:
 - This technique was developed for petroleum site characterizations where benzene is the major VOC of interest, and the method does not yield representative results for chlorinated VOCs.

- The method does not account for permeation rates of PCE or other VOCs that occur through the bag material as the samples are warmed.
- For PCE and other chlorinated VOCs, the lower solubilities from these chemicals and greater K_{ow} results in significantly lower concentrations of PCE in solution and consequently less PCE is available to partition into air.
 - i. For unsaturated soil, the vapor pressure of PCE is five times lower than benzene, an order of magnitude lower than cis-DCE and two orders of magnitude lower than VC.
 - ii. In saturated soil, K_H for PCE is higher than it is for benzene but the solubility for benzene in water is twelve times greater than PCE and what PCE is present in solution is more likely to partition out of solution onto soil particles.

See [“Soil Field Screening PID Results vs. Laboratory Analytical Results”](#) for a case study demonstrating why not to rely on the bag headspaces screening technique.

- Do not rely on the “1% rule” (a historical viewpoint that if the concentration of a chlorinated solvent DNAPL exceeds 1% of its compound-specific solubility in groundwater, then that compound is likely present as a DNAPL) for the presence or absence of DNAPL. This is not a reliable assumption as it can be falsely positive or falsely negative, and this “rule of thumb” does not provide guidance on how far upgradient the DNAPL source zone is located. Instead, use a multiple methods approach to evaluate DNAPL presence or absence.
- Do not assume that a substance (i.e., solvent) released was clean or pure. Many solvents have preservatives or additives to compensate for undesirable chemical properties (for instance, some chlorinated solvents are photo reactive, and some manufacturers added a small amount of 1,4-dioxane to inhibit photodegradation.) In addition, used solvents tend to have impurities dissolved in them (other solvents, oils, greases, other chemicals, etc.). As a result of this, the physical-chemical properties of the DNAPL may display subtle differences from the published values for the pure substance. To account for this, collect multiple discrete samples of the DNAPL (if possible) and samples of the contaminated groundwater and analyze for parameters that could affect the subsurface behavior (e.g.: dynamic viscosity, interfacial tension, specific gravity, effective solubility, chemical composition, wetting characteristics, etc.)
- Do not assume aquitards are impermeable to DNAPL. This leads to underestimation of fate and transport.
- Do not rely on decreasing concentration trends in high permeability zones as rationale to stop collecting data. This is important because mature or late-stage DNAPL releases may exhibit low concentrations in high permeability zones while exhibiting relatively higher concentrations in the underlying low permeability zones.
- Do not rely on monitoring wells to characterize a site, including identification of DNAPL zones. Monitoring wells can easily miss discrete DNAPL zones, long well screens intersecting ganglia or thin DNAPL lenses can result in a diluted sample that does not show contamination, and (depending on site-specific conditions) can fail to provide a clear indication of nearby DNAPL mass. Use the [Tool Selection Worksheet](#) to identify appropriate investigation techniques. Monitoring wells may be used for remedy performance monitoring and long-term monitoring. However, well locations and screened intervals should be determined by carefully evaluating the data acquired during site characterization.