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## LNAPL/Petroleum Guide

The section presents guidance for preparation of a Conceptual Site Model for Light Non-Aqueous-Phase Liquid (LCSM) that is adequately comprehensive for decision making regarding the initiation, continuation, or cessation of remediation, and/or long-term management of contamination in place. Preparation of an LCSM and decisions regarding the need for active remediation or long-term management will necessarily be site-specific. The guidance presented is intended, however, to provide a useful starting point for preparation of a final LCSM and discussions with the HEER Office.

The quality of site decisions depends on the quality of site conceptual models. Site decisions are based primarily on current or potential future risks to receptors but can also include a need to ensure that full remediation of a site is completed within a specified timeframe. The latter might include an anticipated need for redevelopment of the property in the near future and a desire to fully remediate the site while resources are available. Owners of properties contaminated with LNAPL by lessees or releases from offsite sources may also want assurances that remediation will take place within a reasonable time frame to minimize interference with future redevelopment and to limit future risks and liabilities.

Cost is also a factor regarding the amount of remediation required at a site but is not the most important one. Doing nothing is the least expensive remedial alternative but is not protective of human health nor the environment in many cases.

This LNAPL guidance is based on the context of the *LNAPL Guide Companion Document* (Companion Document) prepared by the HDOH HEER Office and is attached as an appendix (Appendix A) to this section (HDOH 2018). The companion document provides references, detailed explanations, and the rationale for methods used in this guidance to enhance the understanding of the user. The *LNAPL Companion Document* was specifically created to enable the user to develop a comprehensive LCSM using data routinely collected during site assessments and groundwater monitoring events. As described below, use of this data beyond the presentation of a simple summary table is required for preparation of a LCSM that is appropriate for long-term, decision making. HDOH emphasizes the need for graphic displays of data in the form of maps and graphs, especially for complex sites such as fuel terminals where there are often multiple releases at different times. The goal is to establish a comprehensive picture of what the release conditions were, where the likely initial (primary) source areas were, and how the release progressed in time and space, leading to identification of potential secondary source areas and contamination in different media (soil, groundwater, surface water, sediment, vapor). This will affect where potential receptors may be exposed and where remediation should be targeted (driven by source area, geology, and chosen technology). The guide also discusses more advanced data collection for instances where a more detailed understanding of LNAPL release conditions, risk, longevity and selection of optimal remedial options is required.

The information presented here and in the Companion Document should be used together with information regarding TPH assessment in Section 9.3 of the TGM, the HEER guidance document *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (HDOH 2017 or as updated), and the HEER guidance document *Long-Term Management of Petroleum-Contaminated Soil and Groundwater* (HDOH, 2007). These guidance documents will be especially useful in defining remediation endpoints for

petroleum contamination. To aid with the preparation of LCSMs for sites, HDOH HEER also developed checklists for tiered sites that include a list of desired graphic illustrations (Appendix B). HDOH HEER will use these checklists to review LNAPL documents and to evaluate the comprehensiveness of LCSMs. The checklists also will help identify data gaps in the LCSM.

## **LCSM Structure and Content**

The goal of the LCSM is to describe the nature, geometry, and setting of the LNAPL and daughter plumes (dissolved and/or vapor phases). This needs to be done in sufficient detail to address questions regarding potential environmental hazards or “risks,” future threats, longevity, and amenability to remedial options. Common risks or “environmental hazards” posed by the presence of LNAPL in soil or groundwater water at a site include (HDOH 2017 – EHE GUIDANCE; see also TGM Section 7.6, Section 9.3 and Section 13):

- Short-term vapor emissions (including methane), sheens, ignition of vapors, etc., when the contamination is disturbed during redevelopment or subsurface utility work;
- Long-term vapor emissions to overlying or nearby buildings or migration of vapors into utility corridors or other preferential pathways (ignition hazard)
- Migration of free product (or contaminated groundwater) into surface water or storm drains, other utility corridors, or other preferential pathways;
- Ongoing source of groundwater contamination and potential offsite migration onto adjacent properties or nearby, surface water habitats;
- Unanticipated need for on-site or off-site management and disposal of contaminated soil or groundwater during redevelopment or subsurface utility work.

Risk can change based off of two factors: 1) time and 2) redox environment (aerobic/anaerobic). In the initial release stage, the main risk driver might be LNAPL mobility and offsite migration, whereas the risk driver in later plume stages may be long-term, offsite migration of a dissolved-phase plume in groundwater/surface water, by simple VOC emission from LNAPL or contaminated groundwater to surface or indoor air, or by methane and volatile organic compound (VOC) production during anaerobic degradation (e.g., Hostettler et al., 2007). It is important to analyze the current state of the contamination as well as to describe the dynamics at the site that influence determinations of current and future risk (e.g., tidal changes, seasonal changes in groundwater concentrations and LNAPL thickness measurements, LNAPL gradient, plume stage, dominant redox environments and degradation processes).

Practical questions to be answered by the LCSM should include:

- What plume stage does the LNAPL distribution correspond to?
- Where are the areas of free LNAPL and where are areas of residual LNAPL?
- Is the LNAPL plume mass well defined in three dimensions, so that it can be targeted for remediation?
- Is LNAPL mobile? And if so is LNAPL migrating? If it is migrating, does it threaten any receptors?
- What is the extent of secondary vapor plumes and dissolved-phase, groundwater plumes above levels of potential concern?

- Is there a potential for chemicals of concern (CoCs) to reach receptors at levels that pose hazards?
- Which portions of the LNAPL are serving as long-term sources for high-risk, secondary groundwater contamination and vapor plume generation?
- Is there evidence for natural attenuation and degradation and if so, what is the current and predicted future stage of degradation?
  - What compounds are least susceptible to natural depletion and degradation and likely to drive potential long-term risks?
  - What area and mass of LNAPL can be safely managed in place and allowed to degrade by natural attenuation or natural source zone degradation (NSZD) without posing unacceptable, short- or long-term risks?
  - What are the degradation rates and timeframes by degradation?
- How is degradation/attenuation anticipated to affect short- and long-term risks over time?
- Which are the best areas to target for remediation based on main free product/main mass of contamination location and geology of the site?

If imminent threats are present, then expedited, interim mitigation measures will be necessary while long-term remediation actions are discussed and prepared. (e.g., does the ratio of TPH-metabolites to total TPH increase with time towards the plume center or the area of the more efficient aerobic degradation; does migration risk decrease with time; does vapor or methane production with time increase vapor intrusion or explosive risk during anaerobic degradation and become the dominant risk after migration has stopped).

The general components of an LCSM are listed below. The importance of each depends on the site setting and release context. In some cases, information useful for the LCSM construction may be unavailable or poorly constrained. It is critical to recognize where important gaps in understanding exist so that the decision-making framed by the LCSM is as robust as possible. Where an aspect is unknown or under-characterized, but has little effect on the decision outcomes, its absence would have no appreciable effect on the LCSM.

1. General site characteristics;
2. Hydrogeologic conditions;
3. Hawai'i specific considerations;
4. LNAPL release conditions and characteristics;
5. LNAPL plume delineation;
6. Assess LNAPL mobility and migration, & assess the plume stage;
7. Identify potential receptors of contamination;
8. Use the LCSM to determine potential risks, as indicated.

Release concerns can vary widely between sites based on product type and nature of the release, the hydrogeologic setting, current and future receptors and other factors that govern the fate and transport of the released product and the risk posed to human health and the environment. A small, one-time release of LNAPL in a high-risk situation with a complex hydrogeologic setting might require significantly more data and evaluation than

a large-volume release of heavy product in a simple regime with no nearby receptors. In general, data requirements increase with plume geographic expansion and risk potential, but recognize that requirements could vary significantly under different site circumstances. The HDOH HEER Office strives for consistency between sites, but requirements will be case specific.

### ***Level of Effort and LCSM Tier***

The level of effort to determine each LCSM component is guided by the site complexity and potential risk (Figure 1). Based on site complexity and risk, sites can be categorized into different tiers with Tier I sites being the least complex sites that pose the least risk and Tier III sites being the most complex sites that pose the highest risk. The categorization into Tiers is site specific, but the following examples can be used as a general guideline:

1. Tier I Sites: These are sites with small , one-time releases where LNAPL and dissolved-phase plumes have not migrated offsite and are not commingled with other releases. Examples include a relatively limited and localized release of fuel from an underground storage tank (UST). To qualify for this category, the plume should not be situated above an unconfined, shallow, drinking water resource, be located greater than 150 meters from surface water, be located in a commercial/industrial area and not pose significant vapor intrusion risks to existing buildings. These types of sites have safe access where soil, groundwater and soil vapor can be easily sampled. Most Tier I sites can be addressed through use of existing site data, with interpretation and assimilation of all relevant information into the LCSM.
2. Tier II Sites; Although the release(s) is still relatively localized, these sites are more complex and pose a greater, potential risks to receptors. This may be driven by proximity to receptors; the size, age and complexity of the LNAPL release(s) or related factors that complicate rapid characterization and mitigation of initial risks in comparison to Tier I sites. Tier II sites often require data in-filling, more advanced data interpretation/mapping, or other actions to fill gaps regarding potential threats to receptors. Examples include the release of product from a UST to shallow groundwater (<15 feet below ground surface) and an associated, potential vapor intrusion risk to an overlying building or the potential migration of LNAPL into a surface water body or storm drain.
3. Tier III Sites: This category includes large, petroleum handling sites (terminals, refineries, military fueling, etc., with histories of multiple releases, widespread contamination, intermingled plumes and with high potential for plume migration. These sites can pose significant, vapor intrusion risks for onsite or offsite buildings, particularly if groundwater is relatively shallow. An increased risk is posed for sites located above unconfined, drinking water and within 150 meters of a surface water body, or adjacent to a residential area. Full characterization of the site might be complicated by buildings, subsurface utilities or access to offsite areas where soil, groundwater, or soil vapor is not easily accessible for sampling. The Tier III sites will require a more advanced level of quantification, modeling, or other scientific

evaluation techniques. The resulting data and conclusions are used to address questions of current and future plume conditions and remediation/management strategies.

#### Data Requirements for each Tier

##### Tier I sites:

- Soil boring and well installation logs (and photo logs, if available) that detail the lithologic character of the subsurface system, including use of both field screening and laboratory analytic data to interpret LNAPL presence and distribution.
- Field observations such as odor staining, free product/sheen observations, paper towel/glove test, or different colors/viscosities of free products;
- Soil, LNAPL, groundwater (including monitored natural attenuation analysis results (MNA)) and vapor laboratory analytical data, and the time sequencing of those data (particularly groundwater sampling over time);
- Fluid level and product thickness observations in wells and the mapped distribution of free product over time at similar water table and under varying water table conditions (for the same wells; hydrographs);
- Physical water quality parameters (include calibration for those parameters).

Existing data for Tier I Sites is sufficient to define the conditions outlined in the LCSM, as listed below. The data can be used to ascertain plume boundaries through time and estimate the 3-D geometry of the LNAPL body (free and residual). Both synoptic LNAPL gauging and groundwater analytic data can be used to indicate if the LNAPL plume and/or dissolved-phase plume are stable, shrinking or migrating. Differing product types can also be identified and assessed separately if more than one release has occurred at the site. This might also be necessary for a Tier II condition. Once the geometry and status of the plume has been established, relevant receptors can be identified, potential short- and long-term risks evaluated, and interim and longer-term measures taken as appropriate.

##### Tier II & Tier III sites:

Tier II and III sites will use the available data noted above and augment that information as necessary to address one or more aspect of the LCSM that cannot be ascertained with adequate certainty. Examples of more advanced data collection, use, and analyses are provided in the LCSM Companion Guide and LNAPL CSM presentation (October 2017) on the HDOH webinar website (<http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/Webinar>) and may include:

- Fuel composition (forensic) or product type analysis
- Petrophysical data (e.g., Pore fluid saturation, capillarity, interfacial tension, specific gravity/viscosity)
- High resolution core photography under white and ultraviolet light
- Laser-induced fluorescence (LIF) measurements
- Membrane-interface probe (MIP) measurements
- Geophysical measurements

- Tracer tests
- Pump, bail down, flow, or other field tests
- Vertical profile sampling
- Tidal study
- Borehole geophysical analysis
- Velocity potential mapping
- Modeling

These examples are not comprehensive, but provide an indication of the types of data and evaluations that might be carried out in more complex situations. As noted, site specific factors will dictate which of these data collection and evaluation approaches are warranted. For instance, a new, large release that directly threatens a sensitive receptor in the near term would not benefit from forensic chemistry, since the nature of the product released is already likely to be known. The site might, however, significantly benefit from multiphase modeling of mobility and transport distances and timing to receptors to optimize the development of an interim or a comprehensive remedy to minimize migration.

## **LNAPL Mechanics and Implications**

A multiphase environment is one in which immiscible phases of water, LNAPL and/or vapor compete for pore-space. The behavior of each phase is a function of the capillary pressure between the phases and the physical nature of the pore space and involved fluids. Multiphase LNAPL mechanics are similar to standard hydrogeologic processes, except more complex and transient due to the non-mixing (immiscible) state of the three typical phases of interest. A suite of standard and multiphase parameters affecting LNAPL migration, cleanup, and risk are discussed in the Companion Document and include:

- Relative permeability towards any phase as a function of its saturation
- Intrinsic soil permeability
- Soil porosity
- Phase density
- Phase saturation
- Fluid properties including interfacial tension, viscosity, and density
- Fluid potential gradient

. Phase movement (water, LNAPL, or vapor) in any direction is controlled by the fluid and soil properties and the gradient in that phase at any point in time and space. Those soil properties vary nonlinearly as a function of saturation, pressure and related transient effects.

There are many technical concepts and considerations that should be reviewed to better understand the framing of the LCSM and the implications provided below (see Companion Document, Appendix A). One of these technical concepts and considerations is the use of

effective conductivity and transmissivity. Conductivity and transmissivity are commonly used to describe flow of LNAPL through a formation and are briefly described below. The modifier “effective” means the scaling of these parameters in accordance with the fluids involved and saturation distribution.

**Hydraulic conductivity (K)** is a measure of the ease of a lithological unit to allow flow of (or transmit) a *single* fluid via pore spaces or fractures under a hydraulic gradient ( $dh/dl$ ). Conductivity depends on the permeability of a material, the degree of saturation, and the density and viscosity of the flowing fluid. Conductivity is a key parameter in Darcy’s law (Darcy’s law says that the discharge rate  $q$  is proportional to the gradient in hydraulic head and the hydraulic conductivity ( $q = Q/A = -K*dh/dl$ ), which also can be measured as the flow of the fluid through a cross-sectional area). The average pore velocity is  $q/\Theta$ , where  $\Theta$  is the effective porosity for the fluid phase.

**Transmissivity (T)** is a measure of the capability of the entire thickness of a layer to transmit water. Transmissivity is what is actually measured in most aquifer tests and is related to the average conductivity by  $T = Kb$ , where “b” is the thickness of the relevant hydrostratigraphic unit. Transmissivity is measured in length<sup>2</sup> per time ( $L^2/t$ ). Effective transmissivity (that is measured under multiphase conditions) may be used as a measure of LNAPL recovery potential and mobility (migration). Although it is a useful parameter, it has to be placed in context with the multiphase and hydraulic conditions under which it was measured and how it might be applied more generally. LNAPL transmissivity, unlike groundwater transmissivity, is not the simple relationship of  $Kb$ , because the conductivity varies as a function of LNAPL saturation, which in turn is non-uniform in the formation. Each of the fluids and media can comprise multiple orders of magnitude variability in permeability, viscosity, and saturation in the natural environment. Standard groundwater hydraulic conductivity and transmissivity apply to a single-fluid environment. With the addition of variability in a multiphase, heterogeneous environment, transmissivity can have a large range of variability itself, which becomes even more varied under fluctuating water levels, leading to varying degrees of saturation and residualization (entrapment). Under unconfined conditions, transmissivity has been observed to be small at the high water table and larger at low water levels. Transmissivity measured under non-pumping conditions can often indicate lower recovery than when measured during pumping conditions. Transmissivity measured one day by one method may differ by orders of magnitude from transmissivity measured on another day by a different method (Beckett and Huntley, 2015).

Therefore, transmissivity in a multi-phase, heterogeneous environment is a complex parameter and attempting to tie mobility and LNAPL recovery to a specific threshold number of transmissivity is oversimplifying a complex environment. When using transmissivity as an indicator for mobility, migration, or recovery, the context needs to be provided so that limitations of the transmissivity data interpreted are known.

Different petroleum products can have very different transport, flux, risk, and cleanup contexts. Light-end products, such as gasoline, are more mobile in the subsurface and have

the largest dissolved-phase and vapor phase plumes and fluxes. Heavy petroleum products like marine bunker fuel or other oils have much less mobility in the environment, both as free-phase (Figure 2) and in the associated dissolved- and vapor phases. These same properties cause heavier oils to have a high persistence and lifetime in the subsurface environment and make them more difficult to remediate. However, due to the lower mobility and lower potential to produce vapors (except methane and other vapors (e.g., aliphatics) potentially produced by methanogenic degradation), heavier products represent a smaller environmental risk (with exceptions) than lighter fuels.

Key multiphase implications affecting the LCSM construction and technical thought process are outlined below. Note that while the LCSM is in part "conceptual" by definition, certain aspects are quantitative.

1. In Hawai'i, the presence of fractured bedrock, boulder alluvium and unconsolidated coralline deposits in subsurface strata suggest that LNAPL migration rates can, under some conditions, be quite high, even potentially greater than groundwater flow velocities. Immediate measures to address a new release are therefore of very high importance to control migration of the product as quickly as possible.
2. The migration of fuel in coralline deposits in many ways parallel that of fractured rock systems, but at a smaller scale and with more discontinuity. One aspect of LNAPL behavior in corals, limestones, and mafic rock (aka basalt) is that there is a tendency for these materials to be "oil-wet." That means that LNAPL moving within these materials has a higher likelihood to become permanently trapped as it passes through the matrix. This is caused by a natural affinity of petroleum to calcareous material. This factor also makes cleanup more difficult as the residual mass will often be stored in the smallest pore spaces of the overall matrix. Furthermore, the change from "water-wet" to "oil-wet" can be transient, highly irregular, and not marked by a sharp boundary, making LNAPL movement within coral deposits more difficult to predict and characterize. Because of its prevalence in caprock sediments or fill material below the water tables and outside most drinking water zones, releases to coralline strata, while complex, primarily threaten surface water bodies and are of less concern to drinking water supplies than releases to fractured, volcanic rock systems.
3. LNAPL from gasoline releases usually spreads to a larger lateral extent in comparison to releases of middle distillates or heavy oil due to a lower viscosity/density and a resulting higher mobility of the product (Figure 2). The higher viscosity and density of diesel and heavier fuels limits their mobility in comparison. Releases of these fuels can, however, cause LNAPL to be distributed to a greater depth due to the inability of the product to spready laterally. This, combined with water table fluctuations, can cause product to become trapped below the water table at potentially significant depths. In addition, it has been observed that diesel fuel typically becomes more emulsified in groundwater, presumably due to enhanced bacterial degradation (less toxic to biota in comparison to gasoline). Lastly, LNAPL releases from diesel or oil spills are more persistent.

4. LNAPL release gradients and associated saturation drive relative mobility. The greater the gradient and associated saturation, the more mobile the product. Residual saturation is a function of the initial LNAPL saturation and the properties of the soil and LNAPL. The higher the initial saturation, the higher the residual saturation. The immediate source area of the release will generally have the highest residual saturation.
5. After the initial release, the source area LNAPL gradients and well thicknesses will both diminish through time due to migration and diminishing release pressure. As the LNAPL well thickness in the source area dissipates, the leading edge of a mobile LNAPL plume will pass through peripheral monitoring well locations that did not previously exhibit floating product.
6. Most field scale parameters pertaining to LNAPL migration and remediation are transient, changing with time and distribution of LNAPL, which is unlike saturated groundwater flow. Transmissivity, conductivity, saturations and other factors change over time and with changing plume conditions. Because saturation and relative permeability are not constants and have exponential relationships, careful interpretation of data for these parameters is needed and must be put in context temporarily, noting both the timepoint of sampling in a transient environment (e.g., water table at the time of sampling) and plume stage. The initial residual saturation is likewise not a constant but varies with LNAPL saturation/migration history.
7. One-time LNAPL releases become stable incrementally, but generally over time frames of 10 years or less. The older the release, the more likely it is to be stable; (i.e., LNAPL is no longer spreading to a larger area or depth provided that hydrogeologic conditions do not change.) All things being equal, smaller releases stabilize more quickly than larger releases and spread a lesser distance. Lighter products travel farther and faster than heavy products like bunker or crude oils. After a plume stabilizes, the remaining mass (free phase and residual) drives potential long-term risks as chemicals continue to slowly partition from the LNAPL into water and vapor.
8. Under unconfined and equilibrium conditions, the thickness of LNAPL in a monitoring well reflects the interval of the strata that contains mobile (but not necessarily migrating), free-phase product (Lenhard et al, 2018). The total LNAPL thickness in the formation including residual is commonly much greater. The volume of LNAPL per unit area is larger in wells compared to that of a comparable area in strata due to the presence of soil, which occupies part of the volume space. Variation in product thickness reflects mobility under different hydrogeologic conditions such as water level fluctuations (Figure 3). LNAPL thickness in wells can be difficult to interpret particularly in heterogeneous formations but typically do not exaggerate the thickness of the formation.
9. LNAPL will often flow in all directions around a release area due to the radial nature of typical release gradients and strongly influenced by lithologic character, with an additional influence from the ambient groundwater gradient. During the

- early stages of an LNAPL release, LNAPL follows in a more radial gradient than the groundwater gradient). Many LNAPL plumes retain a characteristic, radial migration pattern for long periods after the initial release.
10. Multiphase flow is different from groundwater flow, because groundwater is a single phase with parametric constants (transmissivity, conductivity, storability, etc). As a result, conductivity for LNAPL cannot be derived by dividing transmissivity by LNAPL thickness, as is sometimes attempted. This approach can significantly underestimate conductivity and mobility.
  11. Most porous materials have an entry pressure that prohibits non-wetting fluids (e.g., LNAPL and vapor) from intruding in absence of a sufficient gradient. As the gradient diminishes, further plume movement is impeded by this entry pressure at the lateral boundaries.
  12. LNAPL infiltrates the largest pores first. Fine-grained material like silt can delay the arrival time of LNAPL compared to more porous material because LNAPL movement through small pore throats needs more pressure for migration. This can cause LNAPL to be more rapidly trapped and result in a prolonged contaminant residence time in soil and groundwater. It also causes highly variable LNAPL movement in heterogeneous geologic environments.
  13. The LNAPL effective conductivity diminishes through time as the finite volume of oil is distributed over a larger volume of aquifer material. As this occurs, the overall LNAPL saturation decreases as a function of spreading and the relative permeability of the formation to oil decreases exponentially. This can be accentuated by water table fluctuations that vertically redistribute LNAPL over larger volumes of aquifer/soil materials. LNAPL migration effectively ceases when there is no longer sufficient pressure from the source to overcome the entry pressure threshold at the periphery of the plume, but some of the LNAPL near the source may remain mobile.
  14. Soil has a capacity to hold oil as trapped residual (i.e., residual LNAPL is immobile). This causes a finite LNAPL release to theoretically be retained as residual at some maximum spreading distance from the source area. In practice, this maximum spreading distance is not reached because of the other facets of stabilization. A fully residualized plume will no longer exhibit free-phase (mobile) LNAPL in observation wells, even though the formation remains contaminated with residual LNAPL.
  15. The lack of air-filled pore space below the water table (e.g. due to a seasonally or tidally rising water table) leads to LNAPL being trapped below the capillary fringe. Residual saturation in a two-phase system (e.g., the saturated zone) is generally greater for fine- versus coarse -grained material and as well as for poorly sorted versus well sorted material. LNAPL mobility is reduced as LNAPL becomes trapped below the water table, but risk might be increased due to the higher potential of solubilization.

16. Flux is the product of the effective solubility of a compound and the flow. The effective solubility is the mathematical product of its pure phase solubility and the mole fraction of component in source. Therefore, the effective solubility of LNAPL is always lower than pure phase solubility for single component chemicals (e.g., benzene). The flux of a chemical is also dependent on geology. The more coarse-grained the material is, the higher the flux and the shorter the time to de minimus concentrations.
17. Chemistry affects flux magnitude: the more water-soluble a chemical is, the farther that chemical travels in a given time in water. The less water-soluble a chemical is, the more likely it is to remain close to the source. Such observations can be used to help identify the location of a source, since chemicals in groundwater are fractionated from each other and arrive at a given well at different times according to their solubilities. MTBE and benzene, for example, can travel far from the source and are usually among the first chemicals to arrive at a monitoring well (Stout et al., 2010), indicating a potential release. Benzene arrives earlier but is more transient than xylene. Naphthalene, with its lower solubility is a good indicator of LNAPL location. However, degradation also affects chemistry and is often dependent on the surrounding redox conditions and presence of water. For example, benzene and toluene degrade in a similar manner under aerobic conditions. n-Alkanes also degrade aerobically. Under anaerobic conditions benzene and n-Alkanes degrade more slowly, but toluene can be depleted (Alvarez, 1998).
18. LNAPL in the *vadose* zone drains quickly to a field residual state in a matter of days to a few months following release cessation, depending on field conditions and the nature of the subsurface strata. This is analogous to water percolation through the soil column. Smaller releases might not travel far from the source and instead become trapped in shallow soil.
19. Because LNAPL (free phase plus residual) is the overwhelming mass in a release system with the vapor, sorbed, and dissolved phases being a miniscule percentage, the dissolved phase and vapor phase do not persist without a LNAPL source. Therefore, targeting the source mass is important for remediation of dissolved and vapor plume contamination. Variations in vapor-phase and dissolved-phase concentrations of contaminants can likewise be used to determine the locations of LNAPL source zones because they are expected to be higher near the LNAPL.
20. Residualization and other related processes (e.g., degradation) cause the LNAPL plume to progressively pose a reduced risk for continued, lateral migration.
21. While measurement of the LNAPL transmissivity can provide a rough estimate of potential recovery rates and bulk mobility, it does not singularly indicate whether recovery will have a net benefit in reducing risk. Benefits must be measured by comparing remediation objectives against the mechanisms of a given cleanup method and the total LNAPL mass (free and residual) in the subsurface upon which chemical fluxes and the plume longevity depend upon.

22. LNAPL transmissivity must be interpreted carefully and in conjunction with other lithologic and fluid properties. Two sands can have the same oil transmissivity but significantly different soil conductivities and mobilities (Figure 4). Consideration of saturation and soil property distribution will assist in these interpretations.
23. With aging, redistribution, and residualization, the LNAPL finds its way to its deepest resting point as a function of water table and release/transport history. This results in the LNAPL being submerged below recent water table levels. Many remediation failures are due to inadequately identifying this submerged source and not effectively targeting this zone for remediation. Anywhere the LNAPL has historically traveled should be assumed to have residual LNAPL. This includes the shallowest areas closest to the source of the release as well as the deepest level that LNAPL has been encountered as free or residual product.
24. The *residual* mass of LNAPL cannot be accurately determined from well gauging data (LNAPL thickness). LNAPL in wells only reflects the interval of the strata impacted by free phase (mobile) product and most likely only reflects a small fraction of the total mass present in the formation. Residual mass must be interpreted from soil analytic data, saturation data, and inferences regarding LNAPL transport history and plume geometry.
25. At all but the earliest plume stages, the residual LNAPL mass is greater than the free-phase (mobile) mass. The proportion of residual to free-phase (mobile) LNAPL mass increases with the aging of the plume.
26. Natural mass losses from LNAPL reduce and weather the mass in-place over time, as do engineered recovery actions. These mass losses will tend to reduce overall LNAPL saturation in the subsurface, in turn reducing the potential mobility. The LNAPL chemistry also changes over time through weathering processes, generally reducing plume longevity for many but not all chemicals of concern.
27. If the LNAPL mass is finite, then monitoring data should indicate that the overall mass is reducing over time (e.g., exponentially decreasing groundwater trends) due to the attenuation processes noted above. If this is not the case, then an ongoing release is likely present. Mass can be calculated based on concentration by volume/unit area. Persistent dissolved-phase plumes are LNAPL sourced and can be used to interpret LNAPL conditions. Groundwater data can be used to demonstrate decreasing groundwater concentrations trends. Exceptions are new or ongoing releases or when transport conditions bring impacts to receptors (e.g., preferential pathways). Note that groundwater fluctuations, such as tidal or seasonal impacts, must be accounted for in the interpretation of groundwater data.
28. LNAPL hydraulic recovery becomes much less effective for older plumes than for recent releases. As the mass becomes residualized, LNAPL recovery becomes an ineffective tool for achieving many remedial endpoints and alternative cleanup methods or controls to minimize risk are necessary.

## **Description of LNAPL Plume Stage**

LNAPL will spread laterally to its long-term, maximum extent relatively quickly after a finite release and then slow and stabilize over time. Three conceptual LNAPL plume stages are defined as follows: 1) Migrating and laterally mobile; 2) Transitional slowing and stabilization; and 3) Stable, non-migrating and predominantly residual phase. The older the release, the more likely it is in or progressing towards the final stable stage. The larger the release, the more likely LNAPL will be mobile and migrating for a longer period.

To determine the plume stage as part of the LCSM evaluation, site-specific data is used. Questions to be addressed with site data should include:

- What is the interpreted boundary of free (mobile) and residual LNAPL in the subsurface?
  - Use chemical, petrophysical, qualitative field screening and observational data to interpret this boundary (e.g., Figure 5).
  - This boundary will ***almost always*** be larger than the free product plume boundary alone.
- Is the free-phase LNAPL plume still expanding?
  - Are there any indications of recent LNAPL first arrivals at previously non-impacted locations?
  - Are there any new, dissolved-phase detections at distal locations?
- Is the lateral extent of the dissolved-phase plume stable or contracting, as measured by mapping analysis of plume geometry and center-of-mass over time?
  - Compare groundwater plume maps for targeted, dissolved-phase COCs over time (e.g., TPH and TPH-related metabolites, MTBE, benzene, toluene compared to naphthalene; see TGM Section 9.3.1.1 and 9.3.1.2 for target analytes and indicator compounds, and the use of TPH and TPH-metabolites) and quantify/evaluate those conditions. Note that TPH is an indicator compound and HDOH does not accept data from silica gel cleanup (SGC) data alone - only in combination with TPH data without SGC.
  - Compare the concentration decrease of an organic degradable compound (e.g. TPH) to a conservative tracer (non-degradable/non-reactive compound (e.g., chloride in non-marine environments) to demonstrate shrinking plume by degradation.
  - Quantify relative mass changes through time as a function of those plume decreases (if present; see Companion Document).
  - Look for a decreasing plume mass as it implies a depleting and usually stable LNAPL source for those COCs partitioning to groundwater and vapor.
- Are key COCs depleting in a quantifiable and consistent manner, accounting for water table variability (e.g., tides and seasons) in the evaluations?

Note that in practice, dissolved-phase plumes of petroleum-contaminated groundwater are rarely ever “stable.” Dissolved-phase contaminants will be carried along with migrating groundwater. Contaminants dissolve into groundwater passing through impacted soil and are subsequently carried downgradient with the groundwater. The contaminants will move

more slowly than the groundwater due to temporary sorption to organic carbon, clay, and other particles in the strata. The apparent rate of migration will vary depending on the physiochemical properties of the chemical and its susceptibility to biodegradation. If the rate of degradation (and sorption) is less than the rate of transport, then the contaminant plume will continue to expand. If the rate of degradation (and sorption) is greater than the rate of transport, then the plume will appear to shrink and physically retract back to the source, even though the dissolved-phase contaminant itself is still being transported away from the source with groundwater.

### ***Description of Site-Specific LNAPL Conditions***

The following should be incorporated into the LCSM to describe site-specific LNAPL mechanics. These factors/parameters are described in more detail in the Companion Document and examples of their use (e.g., maps) are provided in the LNAPL CSM presentation (October 2017) on the HDOH webinar website (<http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/Webinar>).

1. **LNAPL release conditions, mass, and distribution in three dimensions:** Differentiate between product types, mobility and remediation characteristics for plumes with different LNAPL petroleum types (e.g., diesel vs. gasoline, bunker fuels, etc.; e.g. Figure 5). Characterize LNAPL distribution relative to geological formations (e.g., Figures 6 to 10)
2. **The gradient of the LNAPL plume over time and differing conditions (e.g., Figure 11):** Note that the LNAPL gradient converges with the water table gradient as the LNAPL thickness diminishes to zero.
  - The LNAPL gradient is simply the atmospheric pressure surface of the LNAPL (elevation of LNAPL surface measured as air/LNAPL interface), analogous to groundwater gradient determinations. The top of the LNAPL can be determined by using an interface probe.
3. **The groundwater gradient over time** (corrected for the presence of free product as applicable  $\text{Product corrected water level (PCWL)} = (\text{TOC} - \text{DTW}) + (\text{DTW} - \text{DTLNAPL}) * \text{LNAPL Density}$ ; TOC = Top of casing; DTW = depth to water from TOC; DTLNAPL = Depth to LNAPL from TOC): Report corrected water level relative to above mean sea level (AMSL) and show the gradient at the highest high tide and the lowest low tide level (Figures 12 and 13).
4. **LNAPL behavior during water table changes, both in map view and as individual monitoring well hydrographs for relevant locations:**
  - Synoptic mapping of the LNAPL plume observations, with a focus on reviewing differing water table conditions (due to tides, seasonal variations, water production, or other fluctuations).
  - Single well hydrographs at key locations showing the LNAPL thickness as a function of the corrected groundwater elevation over time (e.g. Figure 14).
5. **The distribution of free and residual LNAPL over time based on gauging & sampling:** This includes determining a time-constrained plume boundary to assist

in understanding the potential for migration past that boundary (Figures 15 and 16). Note that the example in Figures 15 and 16 shows the maximum observed LNAPL thickness in wells per year; ideally the LNAPL thicknesses or footprint should be compared for different years at the same water level.

6. **The distribution of preferential pathways such as utility corridors, internal and external storm-drain systems** (Figure 17)
7. **LNAPL conductivity and transmissivity** (estimated under differing water level conditions as feasible depending on site conditions.):
  - a. Transmissivity can be estimated by pumping or LNAPL slug tests (a.k.a., bail down tests). The ASTM Guide E2856-13 *Standard Guide for Estimation of LNAPL Transmissivity* discusses several approaches, as does Huntley (2000).
  - b. The transmissivity can be used to estimate the LNAPL conductivity, but can be ambiguous, keeping in mind that two units with the same transmissivity can have differing conductivities (Figure 4) and that a pure average over the LNAPL thickness interval will underestimate that value (see Companion Guide). This is due to LNAPL being commonly distributed vertically across multiple lithologies with different permeabilities. Bail down and pump test across these lithologies will lead to one transmissivity result averaged over all these units. This will lead to an underestimate of the unit that may have much higher transmissivity with potentially mobile or migrating free product.
  - c. Effective LNAPL conductivity can be estimated from petrophysical testing data, but can be artificially low due to artifacts of sampling and testing (see Companion Document and LNAPL CSM presentation (October 2017)).

The above evaluations should be used to determine if 1) LNAPL at a site is stable (i.e., not spreading laterally) or if it has migrated during the site investigation/mitigation process and 2) whether it will remain stable under potential future hydrogeologic conditions.

The potential for high conductivity of LNAPL released to fractured rock and other formations with high, macro-porosity is high on the Islands. Storm drains and subsurface utility corridors can also provide a pathway for rapid spreading of LNAPL away from the original release area. While multiphase mechanics still apply in general, these situations present the potential for high LNAPL mobility and a potential threat to receptors immediately after the time of the release. This is because fracture apertures and macropores often present little capillary impedance toward LNAPL flow and, allow the LNAPL to migrate away from the source area if there is a sufficient gradient. Fractures and voids can also form storage compartments for LNAPL that can potentially be mobilized later under changing water table conditions.

The Companion Document discusses fractured rock characterization techniques to explain LNAPL release sites in fractured rock settings where drinking water or receptors are threatened. The goal of macro-porosity and fracture characterization is to understand the geometry and interconnectivity of flow. Fractures with dead-end pore space may act as a

storage cell, but will not allow wider LNAPL transport, as opposed to fractures with continuity through the broader system. Characterization can be simple or complex, depending on the site and release setting. A good starting point is to observe and map nearby road cuts or erosional features in the same formation in the release area to understand flow behavior. Evaluation of rainfall events and percolation patterns where flow can be actively observed in fractures, bedding planes, clinker zones, lava tubes, tumuli or other applicable small scale or large-scale features can also be of assistance. Of course, this evaluation has the most benefit when the surface feature being examined is closely aligned with the release site (similar elevation, materials, hydrologic setting, etc.). In fractured or tortuous settings, the heterogeneous travel paths of LNAPL cannot be described in a predictive manner.

### ***Use of Dissolved-Phase Plume Data***

Dissolved-phase plumes are inextricably linked to the mass, composition, distribution of the LNAPL released, and the hydrogeologic regime. Dissolved-phase transport results in a halo around the LNAPL source as it spreads in all directions, but will be extended in the groundwater gradient direction with only dispersive mechanisms causing lateral and upgradient spread of dissolved-phased contaminants away from the source area. As such, dissolved-phase plume data over time can provide a compelling line of evidence for LNAPL plume conditions. In many cases, when combined with other site data, such observations can be an indicator for plume stability or contraction.

Groundwater analytic data collected at multiple locations should be generated for release sites where LNAPL has migrated to and in some cases below the water table. The following are general effects of an LNAPL release to groundwater and resulting, dissolved-phase plume:

- Persistent dissolved-phase plumes with a stable center of mass frequently indicate the presence of a nearby LNAPL source in contact with the saturated zone, even if no LNAPL has been identified in monitoring wells or soil borings.
- A stable or contracting dissolved phase plume under comparable water table elevations indicates that the LNAPL source is likewise stable or contracting. This is an important observation to note in the LCMS with respect to LNAPL stability.
- If multiple, distinct plume lobes are indicated by the dissolved-phase data then the presence of multiple source areas should be suspected, unless other lines of evidence suggest otherwise. Different sources can sometimes be distinguished by plots of COC or compound ratios (e.g., benzene/xylenes, benzene/trimethylbenzenes, benzene/naphthalene etc., Figure 18) and maximum concentration distributions.
  - Concentration ratios contrasting more mobile compounds (e.g., BTEX) versus more refractory ones (e.g., naphthalene) for any given LNAPL type can have great utility;
  - Comparisons of ratios of compounds relative to differences in solubility and/or vapor pressure can be very useful (e.g., dissolution into water or “water washing” versus vapor depletion);
  - A decreasing ratio of mobile compounds relative to more refractory compounds over time is indicative of a depleting LNAPL source area.

- A new release and/or the migration of LNAPL into a previously unimpacted area can be indicated by a substantial change of ratios in the opposite direction. In those cases, it is useful to investigate if a drop or rise in water level (seasonal, tidal, or through rapid pumping) may be related to an increase in the ratio rather than a new release (e.g., Figure 19 shows an example of rise in B/X ratio with rise in water level, which may relate to tapping a shallow source during high water table elevation). Rapid dewatering of a well during groundwater purging or sampling may lead to displacement of water by air in a shallow formation leading to increased mobility of LNAPL and the formation of droplets of LNAPL on groundwater in the well.
- Different release types (e.g. gasoline versus diesel, or recent versus old fuels) should be evident by the differences in the COC chemistry, degradation stage, and fractionation (Figure 18). Different sources of gasoline can also be distinguished by the presence/absence of tetraethyl -lead, ethanol, oxygenated compounds or refining character. COC correlations with depth to water can be indicative of trapped LNAPL within a shallow source at the high water table or draining and inclusion of LNAPL droplets at the lowered water table. The latter can also occur under conditions of rapid lowering of the water table associated with dewatering activities or excessively rapid groundwater pumping during sampling.
- COC distribution in groundwater is dependent upon differing solubilities, volatilities, and susceptibility to degradation (physically and biologically). This results in earlier arrival of more soluble compounds (e.g., benzene, toluene, MTBE, ethanol) compared to less soluble compounds (e.g., ethylbenzene, xylene, trimethylbenzene, PAHs (e.g., 1, and 2-methylnaphthalene, naphthalene, and middle and higher end aliphatics- usually determined as TPH-g, TPH-d, TPH-o) at locations more distal to the plume center. This also results in chromatographic differences between LNAPL source areas and LNAPL in more distal zones.
- TPH-g, TPH-d, and TPH-o data are commonly determined using EPA method 8015. Though useful, there are also caveats with the method. Any organic material with a boiling point within the spectrum of these fractions will be reported as TPH. This includes non-petroleum biological material and polar degradation products. Chromatogram evaluation to detect these interferences is helpful. Polar compounds within the dissolved-phase plume (various proportions of alcohols, aldehydes, ketones, and esters) are usually associated with the biologic metabolism of hydrocarbons. The relative proportions of non-polar to polar compounds typically varies with distance to the plume center. Polar compounds can be removed using a silica-gel cleanup (SGC). The toxicity of hydrocarbon-related, polar compounds is assumed for initial screening purposes to be identical to that of the parent compounds (refer to TGM Section 9 and HDOH Environmental Hazard Evaluation guidance; HDOH 2017). Groundwater data in the absence of silica gel cleanup must be used for comparison to action levels. However, combined TPH and TPH-SGC for TPH-d can assist in determining the general degradation state of different areas of plume and identifying LNAPL source areas. Non-polar TPH-d is expected to be present at increasing higher proportions as a source area is approached.

- MNA-parameter analysis (e.g., for sulfate, sulfide, alkalinity,  $Mn^{2+}$ ,  $Fe^{2+}$ , nitrate, methane) and analysis of field parameters (dissolved oxygen, redox potential, conductivity etc.) can assist in determining plume source zones, as well as provide evidence of degradation processes. The most reducing conditions are typically found near the release source areas (e.g., methanogenic), when all the oxygen is depleted. Water quality/MNA parameters like dissolved-oxygen, sulfate/sulfide, iron/manganese speciation, methane, carbon dioxide and others, when mapped aerially, can help with identifying the location of LNAPL source area(s) as well as the degradation state of the plume. It is helpful to look at degradation parent and daughter products to distinguish depletion of a parent product through degradation from mixing (e.g.,  $SO_4^{2-}$  to  $H_2S$ ; MTBE to TBA). Simple mixing should not lead to an increase in daughter products. To understand the geochemical environment, precipitation, and sorption better (reduction/precipitation /mobilization of metals; production of gases; reducing/oxidizing conditions) it is suggested to use geochemical modeling computer programs such as USGS PHREEQC program (USGS, 2018), which can be downloaded for free for different computer platforms. PHREEQi, available through the same USGS website is a user-friendly interface for the MS Windows platform of the program. The program models groundwater conditions in equilibrium with minerals and gases under given redox and pH conditions not considering bacterial degradation mechanism. It simulates precipitation and dissolution of minerals for a given groundwater condition.
- The same analogous processes and interpretations for groundwater apply to the vapor phase chemistry as well. However, vapor phase data is not collected in a systematic synoptic manner like groundwater data, so it is more limited in interpretive evaluations. Where available, however, vapor can be utilized for the identification of LNAPL source areas.

### ***Determining Release Character and Timing***

A variety of direct and interpretive aspects of site information and data can be used to evaluate the character and timing of the LNAPL release. Was it a large volume release? Was it a single release or more likely multiple releases, from the same location or different locations? Is the release old or recent? Some of these aspects have been covered previously and those will not be reiterated, but the additional list below can help constrain these factors:

- Is/was the release a recognized event on a certain date and location? While the precise volume of the release is often unknown, the date and type of fuel released is typically known within a reasonable range. For example, on a given date, a pipeline flange failed, releasing an unknown quantity of marine diesel fuel into the subsurface at a given location. The Tier II LCSM in the Companion Guide provides some examples of such reporting.
- Similarly, a review of the history of petroleum operations at a release site can assist in this evaluation component. Is the site a relatively new service station with no prior petroleum handling operations? Is it a military facility with a history of fueling air and marine crafts? Is it a commercial fuel supplying facility only carrying road-

- grade products? Where and how were different fuel types stored (e.g. specific AST/UST and their contents; Figure 20).
- Given the hydrogeologic setting, is the plume widespread or limited, and what are the mass indications in subsurface data? For the same general conditions, a widespread plume has a larger release than a more limited plume distribution.
  - While the rate of release is often unknown, we can interpret site data to assess the likely character of that. For many sites, this factor is not critically important.
    - LNAPL plumes associated with a slow release rate usually do not penetrate as deeply into the aquifer as plumes associated with a rapid, short-term release of like volume. The plume dimensions discussed previously can assist in this evaluation.
    - LNAPL plumes associated with a rapid release rate demonstrate a similar chemical composition throughout, later weathering from the outside-in toward the source area. Plumes associated with a slow release will often have sufficient time to degrade during migration, resulting in a more heterogenous chemistry.
    - Multiple releases at the same or nearby locations will cause changes to the source zone chemistry of the LNAPL and daughter plumes.
    - The general release character is important, sometimes, because the likelihood of remaining LNAPL mobility is in part a function of release recency (or viscosity).
  - Simple and more detailed forensic chemistry can assist in this determination. Fuel refining and character have varied in known ways over time. Certain facets of the original crude oil source are reflected in the refined products (Figure 21). Additives, carbon ranges, and other factors can all assist in the determination of the release age and character. Chromatograms give an indication of the fuel type or types present and the degree of weathering.

## LNAPL Modeling

The preference of the HDOH is a strong reliance on site data and interpretations consistent with the underlying technical processes. However, there are circumstances, particularly at Tier II or III release sites, where multiphase or transport modeling can be useful to depict conditions. Those might include aspects about migration, risk, future conditions, remediation and others.

Multiphase modeling is non-linear and more complex than standard groundwater modeling. Earth materials have a range of 6-8 orders of magnitude for permeability, but that expands by orders of magnitude for multiphase conditions due to relative permeability aspects. Models, whether analytic (simple) or numerical (complex) have several constraining assumptions that go into their formulation. When using a model to support the LCSM, it is important to document those assumptions and ensure they are applicable to site conditions. Results of any modeling should reasonably bracket actual site measurements and conditions.

A common analytic and semi-analytic LNAPL modeling approach is called vertical equilibrium (VEQ). By assuming the LNAPL is at vertical equilibrium, capillary pressures

and saturations can be determined based on observed thicknesses in wells. This approach underlies some of the models produced by the American Petroleum Institute (e.g., API Interactive LNAPL Guide, LNAPL Distribution and Recovery Model [LDRM]), EPA, and others. These approaches work best under simple hydrogeologic systems and tend to fail in more complex systems (highly heterogeneous, variable water tables, multiple releases, etc.; e.g., Figure 3). Use of the VEQ method, or any other model absent of the recognition of its limitations, will not produce fruitful insights. Models are best used to understand processes and sensitivities of certain parameters.

## **LNAPL Remediation**

Remediation goals will depend on the potential risks posed by the LNAPL and daughter plumes, on plume longevity, and site setting, and regulatory requirements (e.g., HAR 11-451- remove/destroy to the maximum extent feasible, and reduction of toxicity, mobility, or volume through treatment, eliminating or minimizing the need for long-term management). The LCSM should be used to prepare an Environmental Hazard Evaluation (HDOH 2017) for the site and identify specific, existing or potential concerns associated with the contamination. This should then be used to develop remedial options and a remedial action plan for the site in combination with a remedial alternative analysis in accordance with HAR 11-451 (HRS-128D) and the nine criteria of the National Contingency Plan (NCP). Green and sustainable remediation factors can be included and evaluated as part of the long-term effectiveness and permanence criteria.

Decisions for remedial action should be based on free product, residual LNAPL, and consideration for both “Total Petroleum Hydrocarbon (TPH)” data and targeted, individual compounds such as BTEX and PAHs. Specific chemicals of concern for different petroleum product types are presented in Section 9 of this guidance. Gasoline-range (e.g., C6-C12) and diesel-range (e.g., C12-C24) hydrocarbons collectively measured as TPH typically drive vapor intrusion risks over individually targeted compounds, although benzene can play an import role in older releases of high-benzene, gasolines (refer to Section 7). The same is true for short-term, vapor emissions to outdoor air due to disturbance of grossly contaminated soil or groundwater as part of subsurface construction or utility work activities.

Hydrocarbon-derived, metabolites generated from biologic processes and included in TPH measurements in the absence of silica gel cleanup typically drive risks for impacts to groundwater as well as leaching of hydrocarbons from soil. Individual, aromatic compounds can play an important role in risk for less degraded plumes in the immediate vicinity of LNAPL. Risk posed by direct-exposure to contaminated soil is normally driven by a mixture of TPH and individual compounds, depending in part on the product released. Other gross contamination concerns (the potential for sheens in runoff from excavated soil, explosion or fire hazards, LNAPL migration into storm water drains, potential for methane buildup, etc.) is again most accurately assessed based on TPH soil, water, and soil vapor data (including methane) rather than data for individually targeted compounds.

A detailed discussion of active and passive remedial actions to address LNAPL contamination of soil and groundwater will be added in the future. Aggressive, initial remedial actions should be carried out to address identified, offsite migration of LNAPL

into nearby surface water bodies or documented, vapor intrusion hazards for existing buildings. This can include sealing of preferential pathways by installing liners into storm drains and/or clay dams within the utility corridor gravel packs. Cracks and utility gaps that penetrate the floor of a building that overlie a significant vapor plume should be sealed and the ventilation system checked to ensure an adequate exchange of indoor air with fresh air.

Long-term remedial actions for LNAPL that will remain in-place due to access or cost concerns include air sparging and soil vapor extraction to remove lighter-end and higher risk hydrocarbons and reduce vapor emission (and explosion) concerns, active or passive removal of mobile LNAPL from individual wells or trenches to reduce further spreading, and the injection of oxygen releasing compounds to impacted zones to enhance natural, biodegradation processes of trapped, residual product.

Remedial and risk management approaches will be needed to address areas where risks are present. One of the most important initial evaluations is the location of preferential pathways and high permeability geological formations such as fractured rocks, sands, coralline deposits, or stream gravel beds. At some sites, mass reduction will be a remedial goal to reduce plume longevity. In some cases, reliance on MNA or NSZD may be appropriate if the plume poses no risk and will be short-lived in the environment. Those are typically small releases (e.g. due to a small release volume, especially for high viscosity products such as oil) with a stable plume outside of drinking water areas and away from receptors of concern.

The LCSM should be used to develop remediation objectives and evaluate which technologies, approaches, and endpoints are most appropriate. LNAPL hydraulic recovery is often of limited benefit, particularly for older and predominantly residualized plumes. Where mass recovery is necessary, this method will not be useful in those situations. Hydraulic recovery is useful to stop LNAPL migration and for mass recovery if it is a recent release. Recovery needs to target the mobile LNAPL and reverse its gradients.

As part of the LCSM preparation, the LNAPL mass and longevity will have been evaluated. From this, ambient rates of mass losses can be estimated, recognizing that those will change over time. These baseline mass loss rates assist in understanding practical remediation expectations. For instance, if the natural mass loss rates exceed those that might be achieved through LNAPL recovery, then MNA, NSZD, or augmentation of those degradation rates may be more realistic.

It is critical that the mechanisms of the remedial approach be consistent with the LCSM and target the LNAPL mass in 3-D. While soil vapor extraction may remove significant mass in some settings, it will do little with respect to targeting LNAPL trapped below the water table. In that scenario, mass will be recovered, but the trend of groundwater COCs will be fundamentally unchanged because a submerged source will still exist.

Finally, some common remedial measures, like radius of influence, may have little relationship to the 3-D targeting of the LNAPL mass. It is important in remedial design and pilot testing that measurements related to the LNAPL targeting be determined and

collected. For an aeration-based method to succeed, it will have to create air-flow through the LNAPL target zones, and that flow can be measured or inferred in the data collection. Modeling of remedial actions can be useful to understand the expected mechanisms and outcomes.

During remediation tracking, it is expected that effective targeting will be demonstrated by increased mass losses in the plume, along with enhanced contraction and chemical changes. For air-based methods, that means a decrease in the volatile constituents of the LNAPL; this decrease will coincide with an increase in biodegradation that can be easily tracked by carbon dioxide production or changes in MNA parameters with inclusion of non-volatile dissolved organic carbon (NVDOC) and dissolved organic carbon (DOC) (Mackay et al., 2018). Remediation tracking will determine when endpoints are achieved or when transition to other methodologies is more useful to achieve the endpoints. Therefore, it is useful to establish a remedial endpoint analysis/exit strategy that proposes potential treatment trains and evaluates different remedial options ahead of remediation initiation or and/or transitioning.

Asymptotic recovery during hydraulic recovery will occur with both efficient and inefficient remedial designs. While an asymptotic recovery curves can be a useful indicator, it will not alone determine remediation success. Plume rebound, and other attributes, indicate failure of the cleanup to target effectively some portion of the LNAPL mass (which feeds the rebound). When assessing success of hydraulic recovery, it is important to look at hydraulic recovery in context of the site such as what area or radius around the system was affected by the hydraulic recovery.

## Summary

This LCSM guidance was prepared to improve site decisions for LNAPL sites on the basis of easy to collect (routine) site assessment data assembled into a comprehensive LCSM. A comprehensive LCSM does not necessarily need additional data collection, but an in-depth data analysis and interpretation of all data collected. Emphasis is placed on interpretation of all data in context with site conditions and sampling methods, including field data collected on a routine basis. Good visual display of data in maps and graphics is necessary to strengthen the LCSM and to enable easier decision making. HDOH HEER provided a tiered approach for LCSM development based on site complexity and site risk. This approach is supplemented by checklists for each tier to help the user identify data and data display needs and data gaps. We hope the user will find this approach useful in preparation of future LCSMs.

## References

Alvarez, P.J.J., Heathcote, R. C., and Powers, S. E, 1998, Caution Against Interpreting Gasoline Release Dates Based on BTEX Ratios in Groundwater.

Beckett, G.D. and Huntley, D., 2015, LNAPL Transmissivity: A Twisted Parameter, Groundwater Monitoring and Remediation.

ESI, 2007. Task 4 – Site Characterization, Former ConocoPhillips Terminal, 411 and 439 Pacific Street, Honolulu, Hawaii, TMK Nos. (1) 1-5-013:010 and 012, September, 2007.

HDOH, 2007, Long-Term Management of Petroleum-Contaminated Soil and Groundwater. Website URL: <http://www.hawaiiidoh.com/tgm-content/1909a.aspx>, June 2007

HDOH, 2017, Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater. Website URL: <http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/EALs>. Fall 2017 and updates.

HDOH, 2018, LNAPL Guide Companion Document, by AquiVer, June 2018.

Hostettler, F. D., Wang, Y., Huang, Cao, W., Bekins, B. A., Rostad, C. E., Kulpa, C. F., and Laursen, A., Environmental Forensics, 8:139-153, 2007, DOI: 10:1080/15275920601180685.

Huntley, 2000. Analytical determination of hydrocarbon transmissivity from baildown tests, D. Huntley, Ground Water 38(1), 46-52, January/February 2000.

Lenhard, R. J., Lari, K. S., Rayner, J. L., and Davis, G. B., 2018, Evaluating an Analytical Model to Predict Subsurface LNAPL Distributions and Transmissivity From Current and Historic Fluid Levels in Groundwater Wells: Comparing Results to Numerical Simulations, Groundwater Monitoring & Remediation 38, No. 1/Winter 2018/pages 75-84.

Mackay, D., Paradis, C., Buscheck, T., Daniels, E., Hathaway, E., de Sieyes, N., Rasa, E, Schmidt R., and Peng, J, 2018, Methods to Estimate Source Zone Depletion of Fuel Releases by Groundwater Flow, Groundwater Monitoring & Remediation 38, No. 1/Winter 2018/pages 26-41, Winter 2018

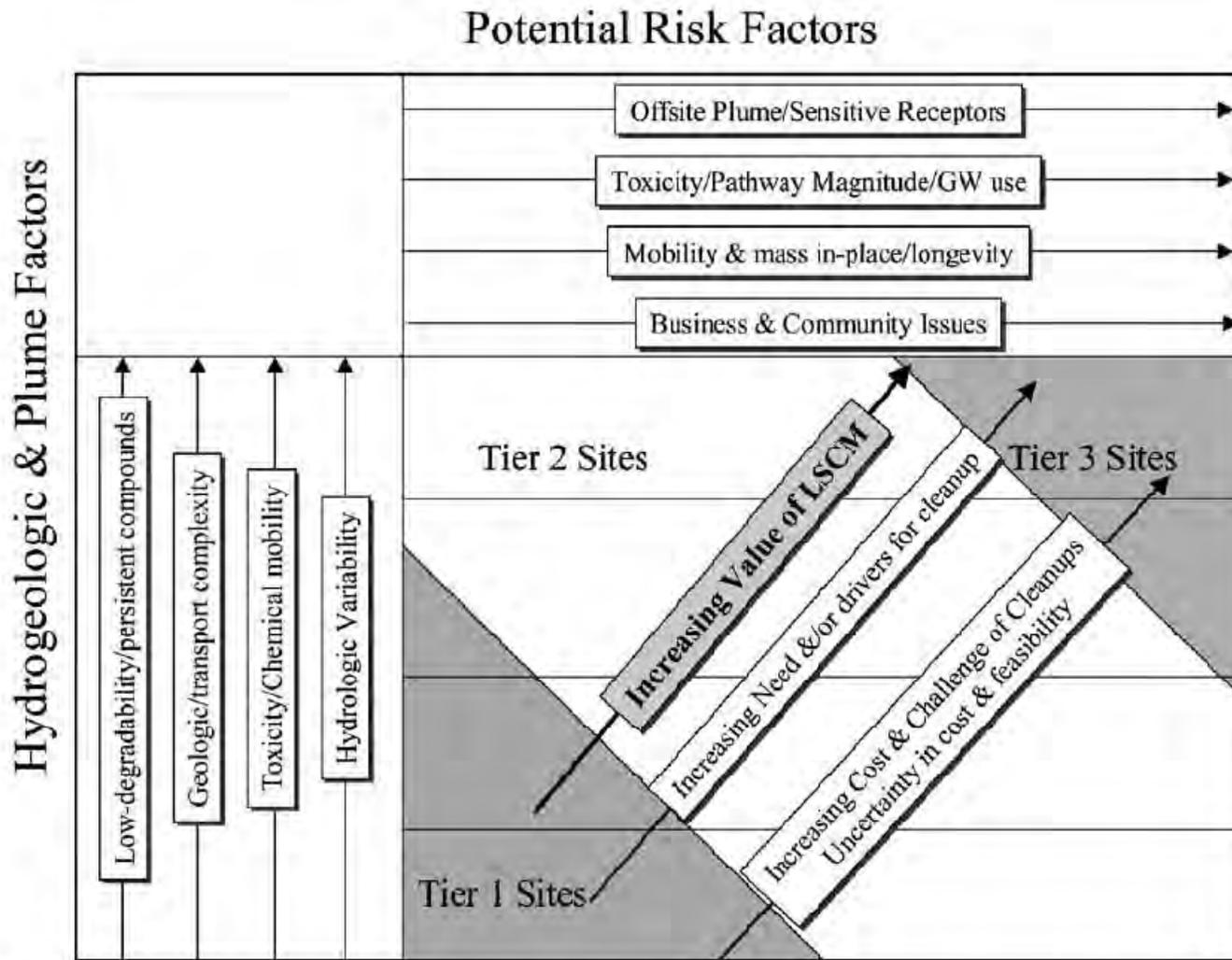
Stout, S.A., Douglas, G. S., and Uhler, A.D., 2010. Assessing Temporal and Spatial Variations of Gasoline-Impacted Groundwater Using Relative Mole Fractions and PIANO Fingerprinting, Environmental Forensics, 11:328-341.

USGS, 2018. [https://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) Accessed July, 2018.

# Figures

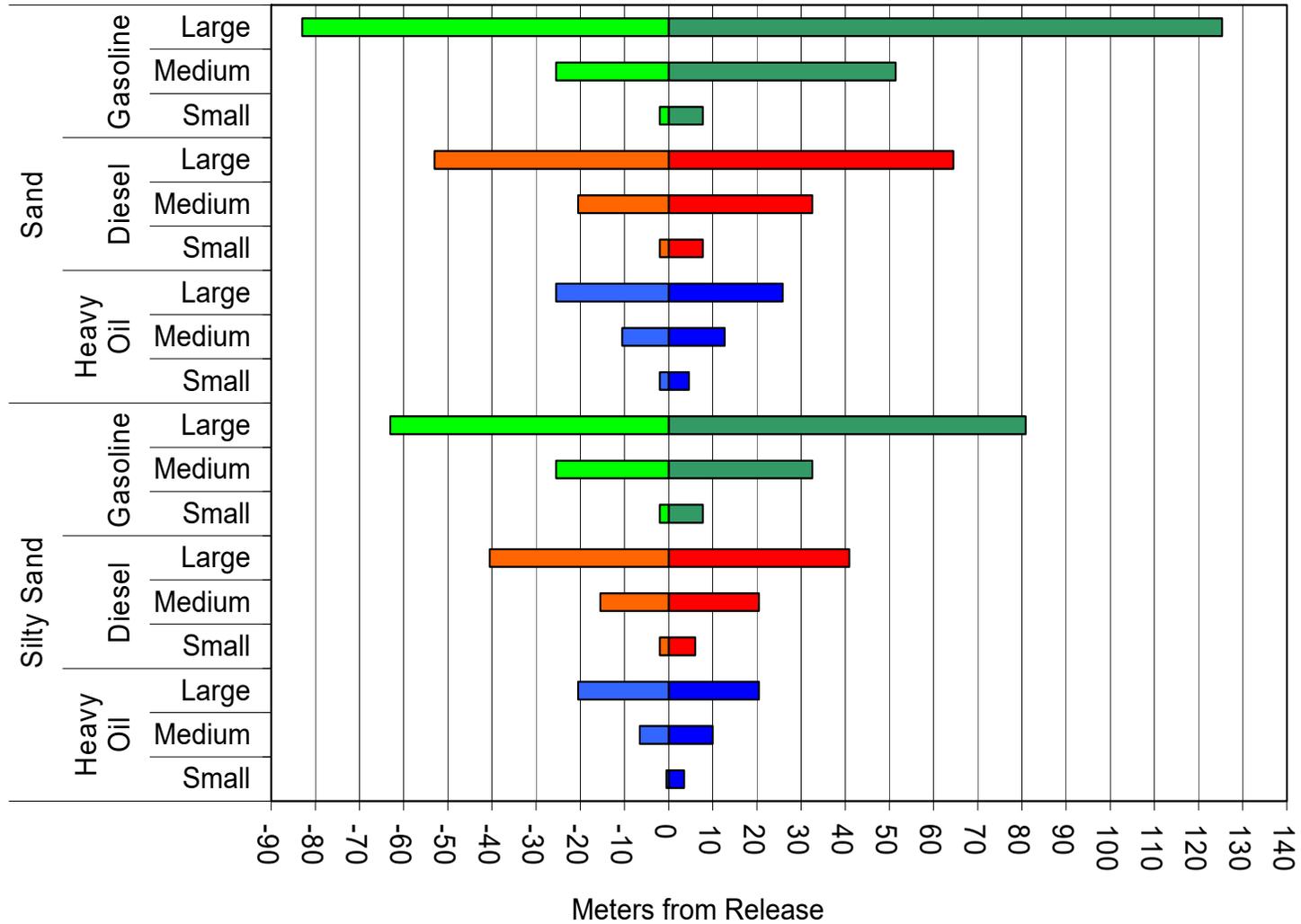


# Figure 1



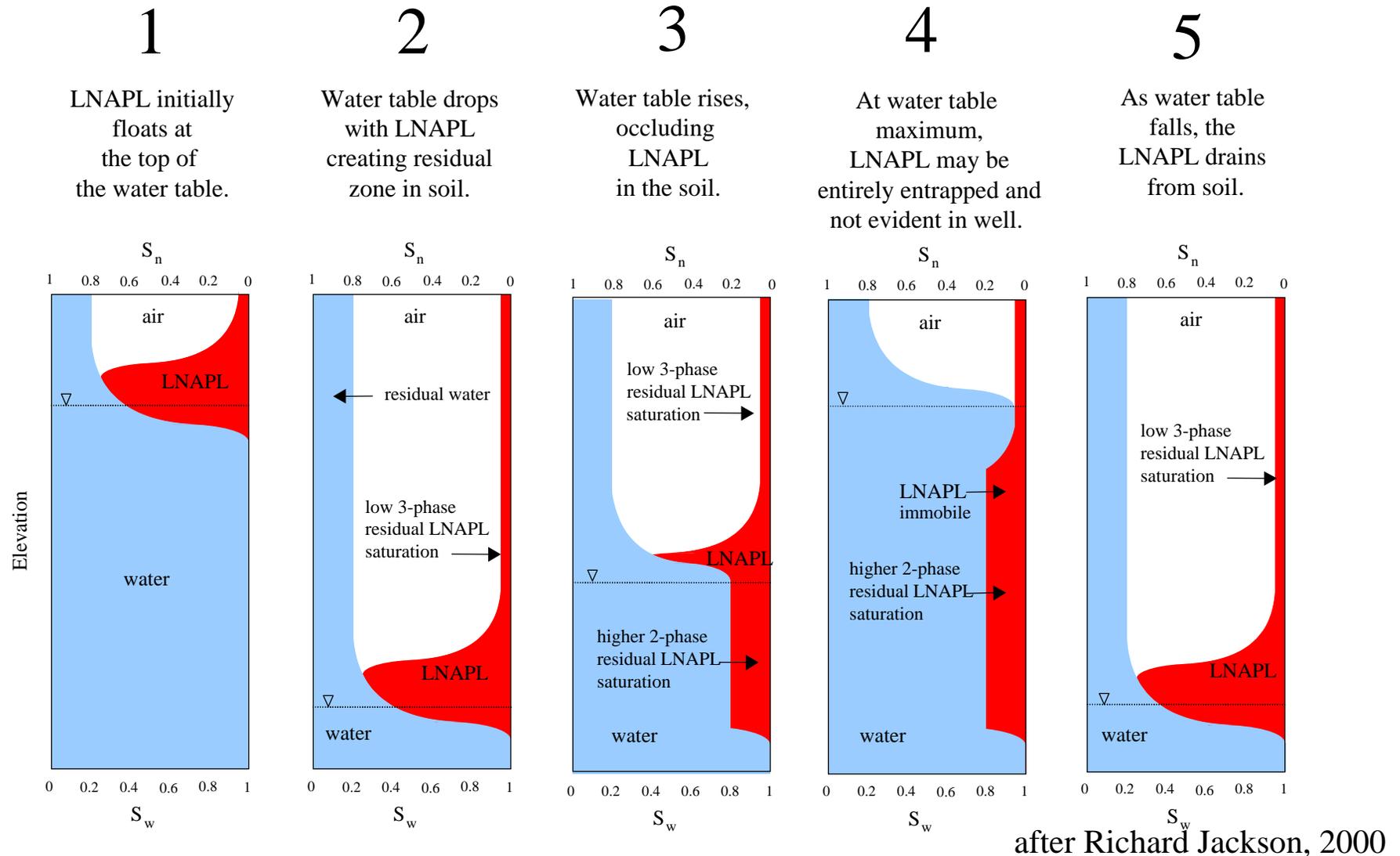
**Figure 1** - Relative Complexity and Value of the LNAPL Conceptual Site Model (CSM). Concept after Tom Sale, 2002.

Figure 2: Comparative Lateral LNAPL Migration  
*(converse is true for vertical migration)*



# Figure 3: LNAPL Thickness Under Changing Water Levels

## *Conceptual Rendering of LNAPL Occlusion*



Note:  $S_w$  = Saturation of water,  $S_n$  = Saturation of LNAPL

Figure 4: Two Sands with Same Oil Transmissivity

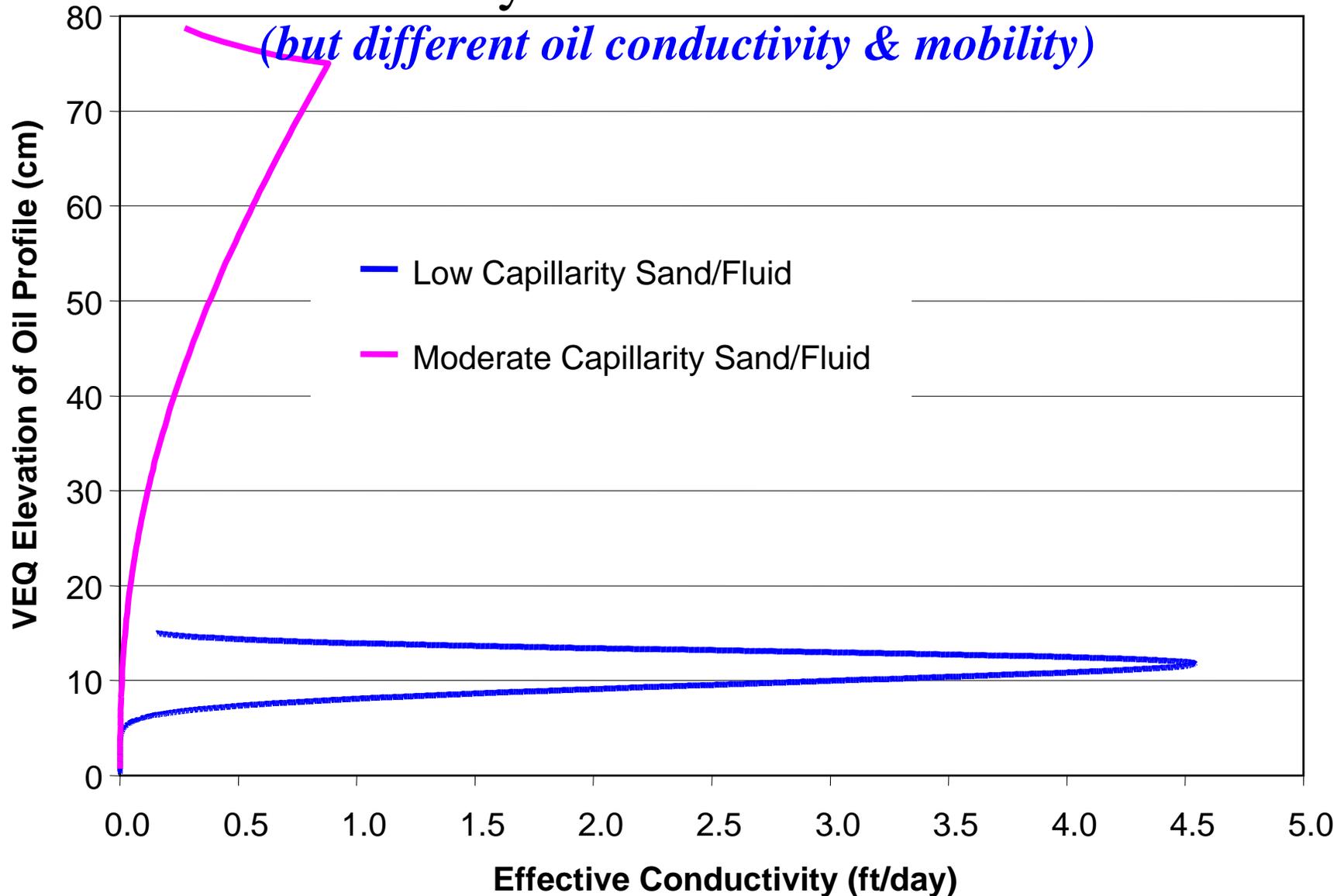
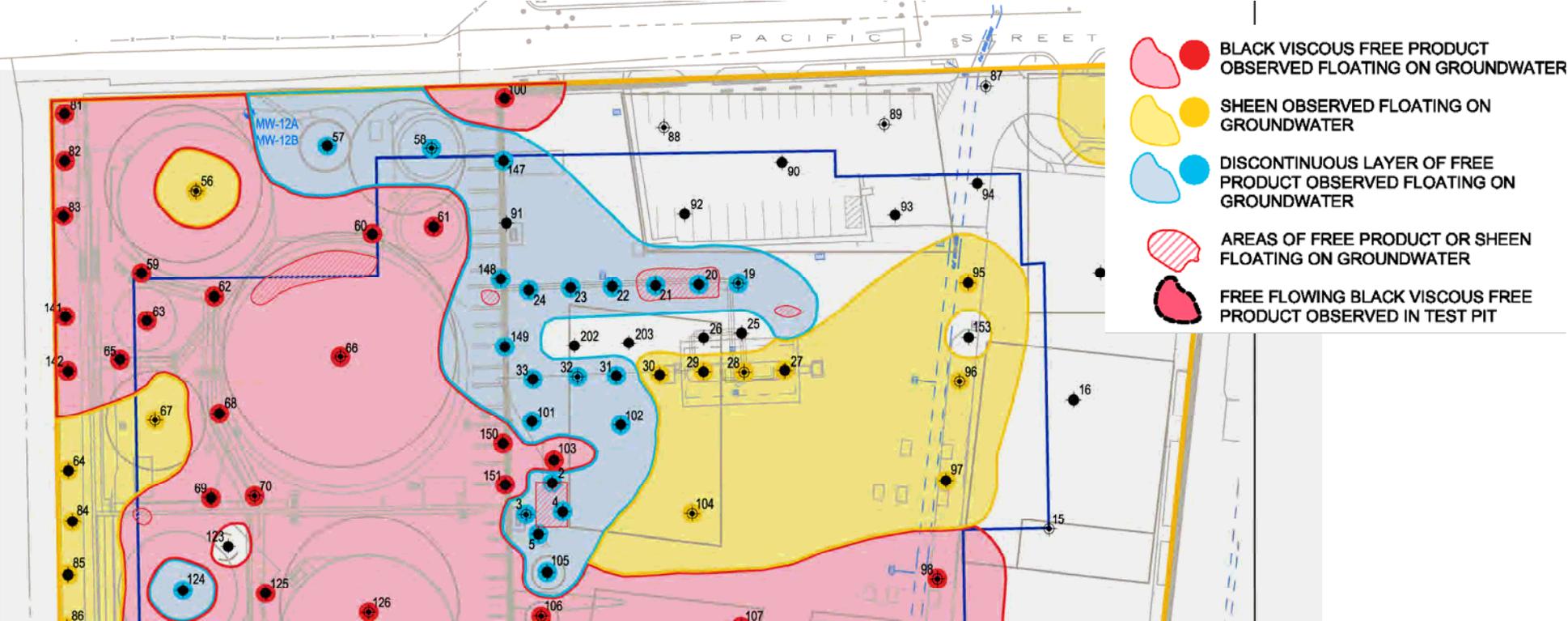


Figure 5: Mapped Free Product Observations Of Different Product Types



ESI, 2007



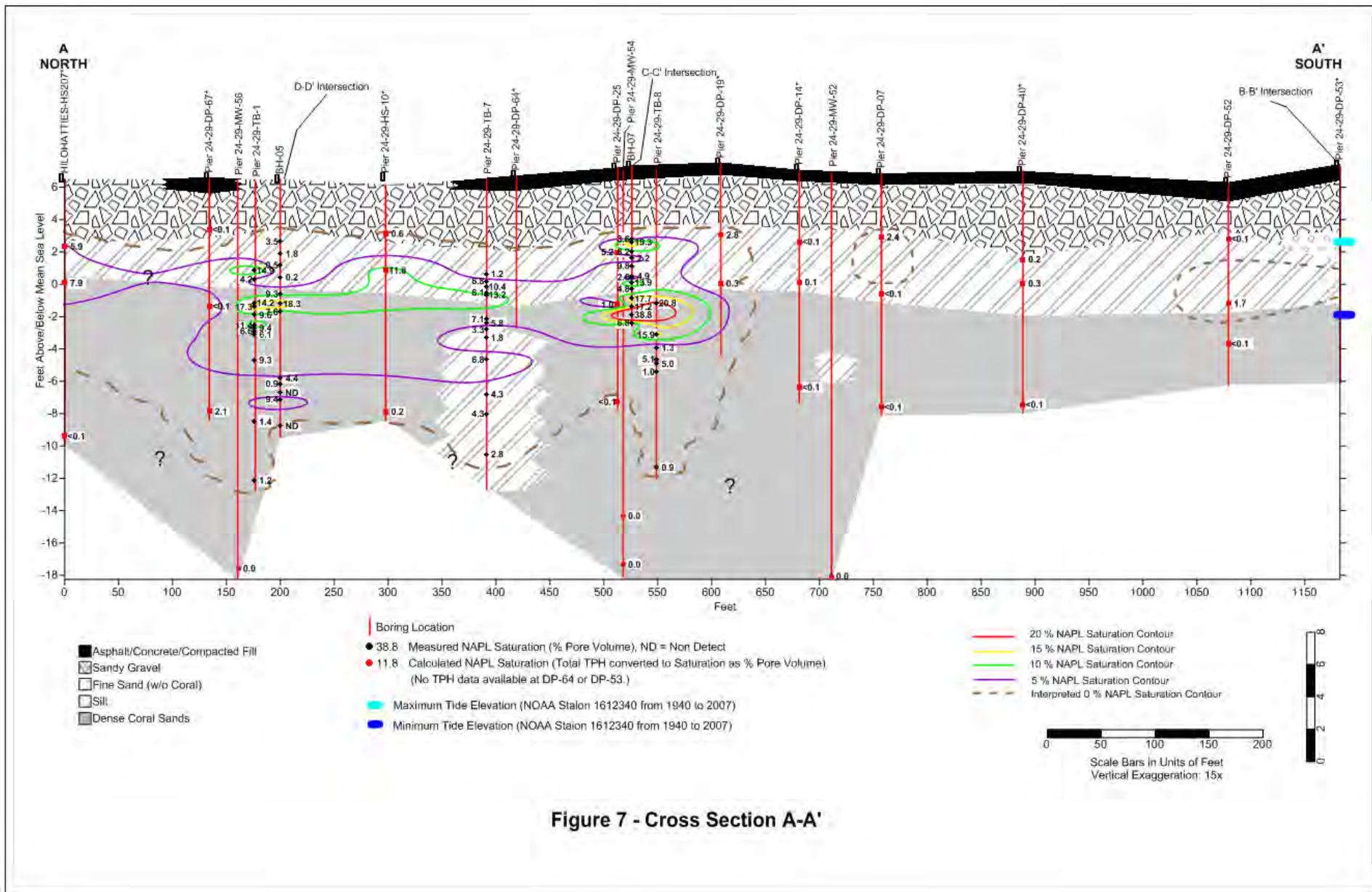
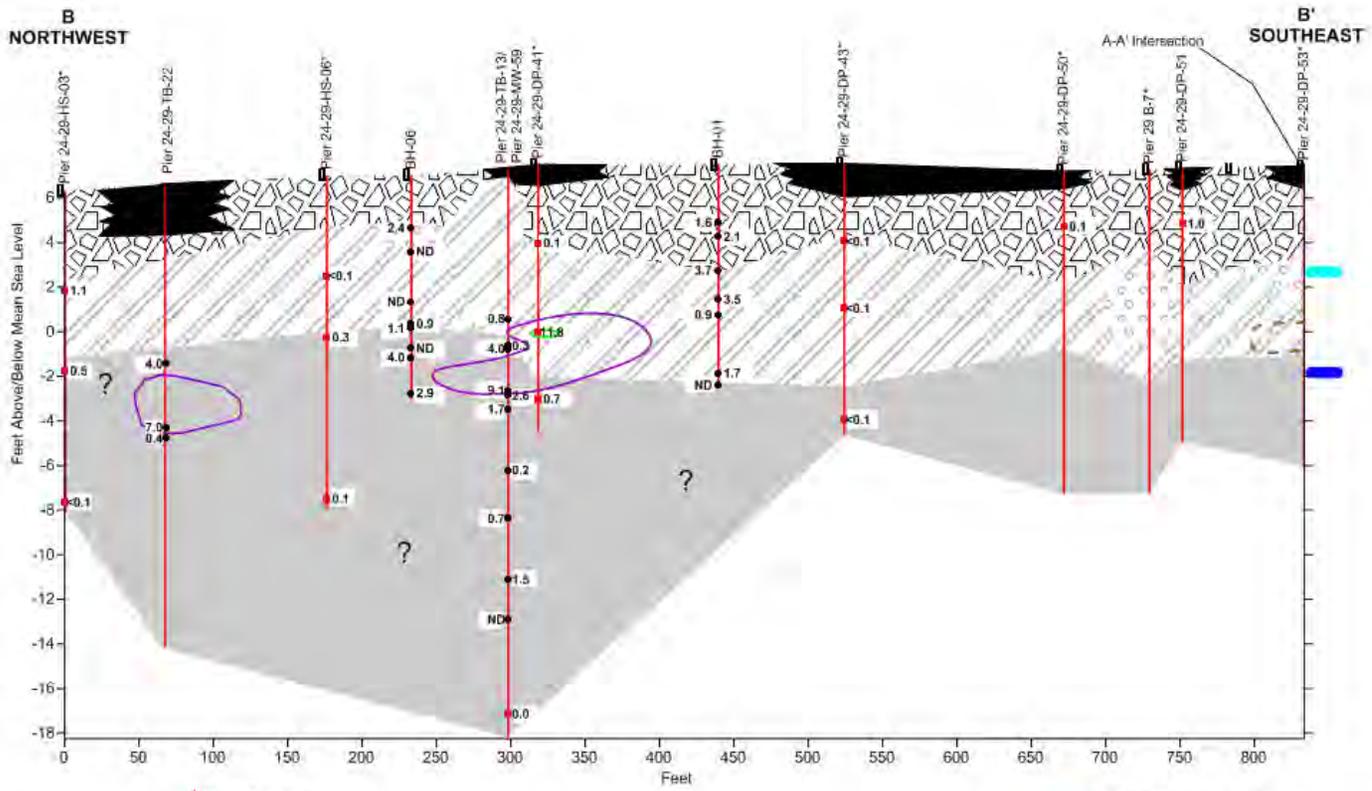


Figure 7 - Cross Section A-A'



- Asphalt/Concrete/Compacted Fill
- ▨ Sandy Gravel
- Fine Sand (w/o Coral)
- Silt
- Dense Coral Sands

- | Boring Location
- 4.0 Measured NAPL Saturation (% Pore Volume), ND = Non Detect
- 11.8 Calculated NAPL Saturation (Total TPH converted to Saturation as % Pore Volume)  
(No TPH data available at B-6, B-7, or DP-53.)
- Maximum Tide Elevation (NOAA Station 1612340 from 1940 to 2007)
- Minimum Tide Elevation (NOAA Station 1612340 from 1940 to 2007)

- 20 % NAPL Saturation Contour
- 15 % NAPL Saturation Contour
- 10 % NAPL Saturation Contour
- 5 % NAPL Saturation Contour
- Interpreted 0 % NAPL Saturation Contour

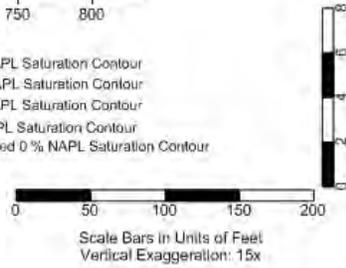
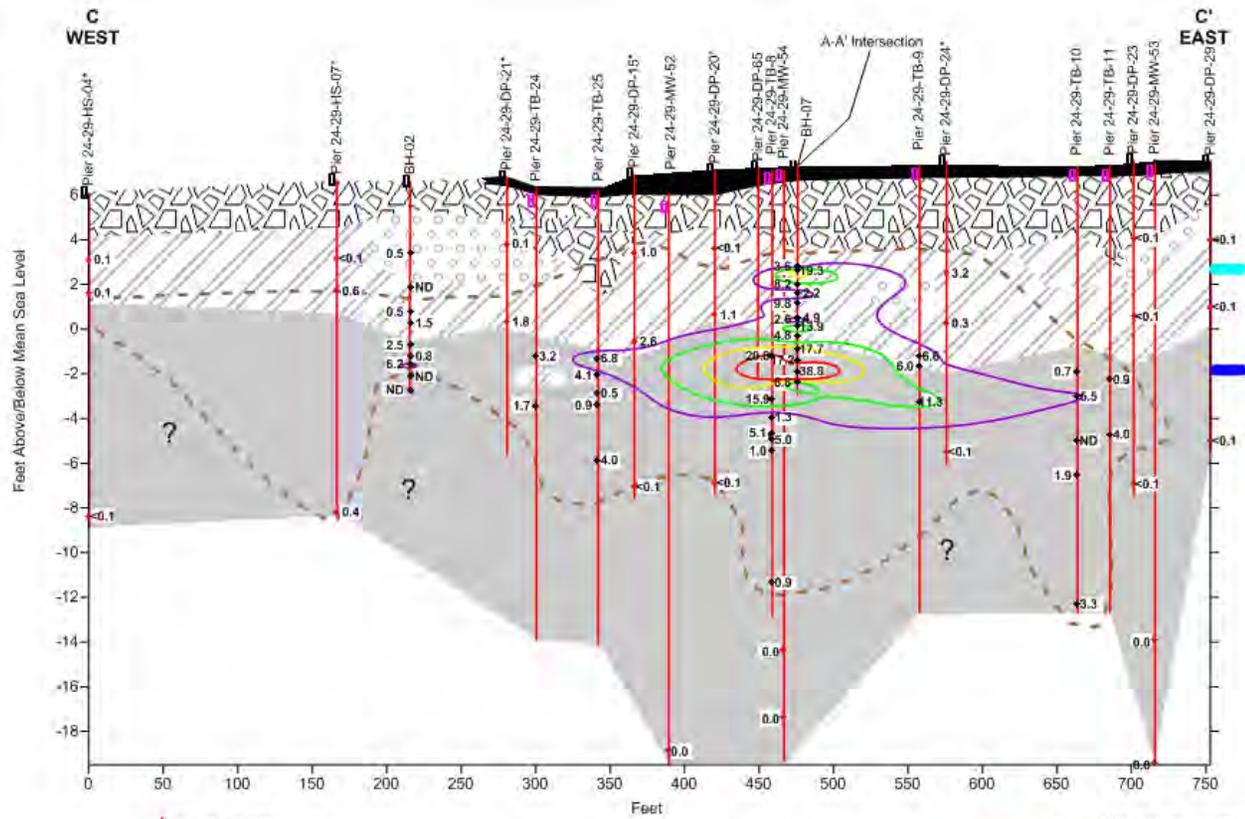


Figure 8 - Cross Section B-B'



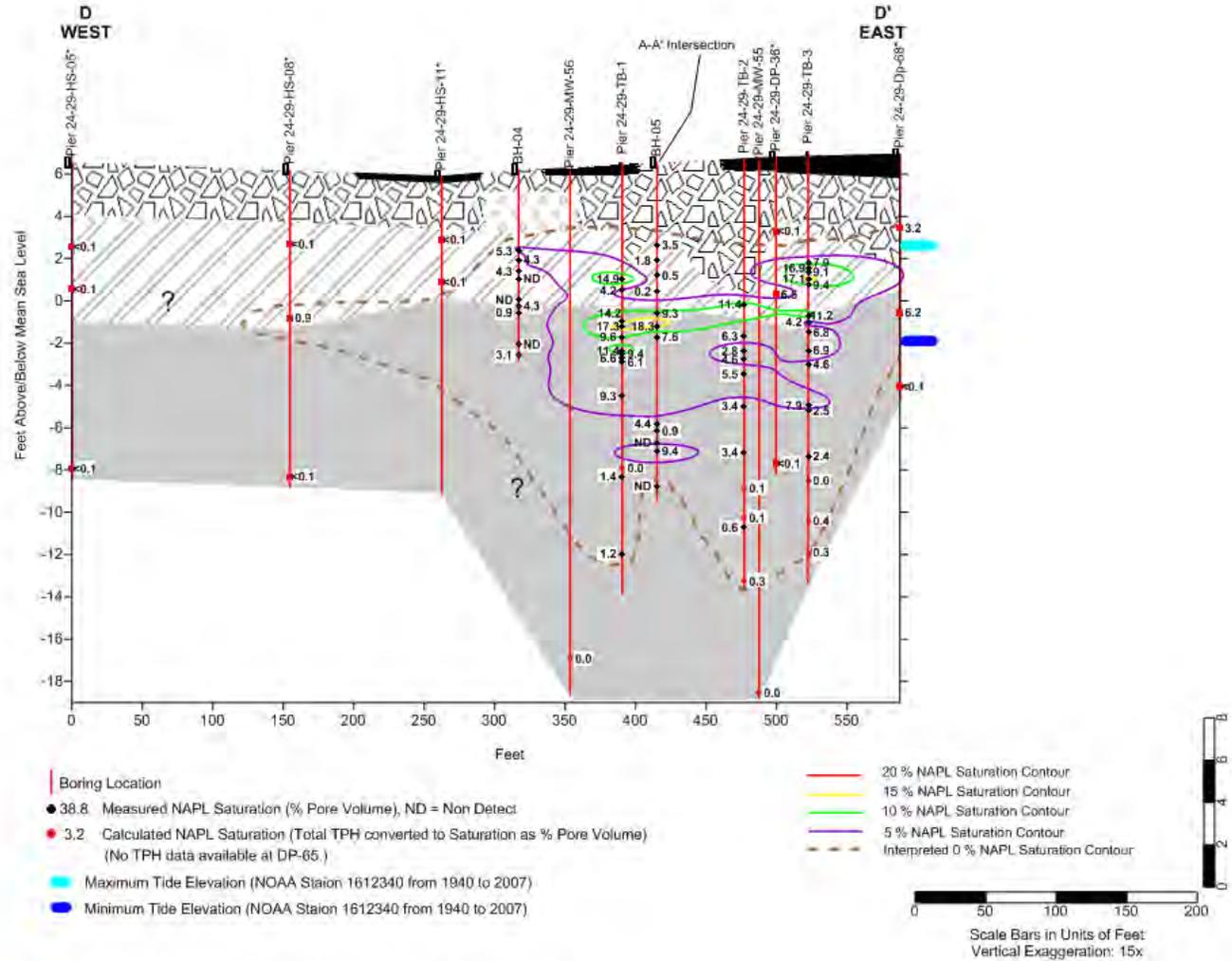
- Asphalt/Concrete/Compacted Fill
- ▨ Sandy Gravel
- Fine Sand (w/o Coral)
- Silt
- ▨ Dense Coral Sands

- | Boring Location
- 38.8 Measured NAPL Saturation (% Pore Volume), ND = Non Detect
- 3.2 Calculated NAPL Saturation (Total TPH converted to Saturation as % Pore Volume) (No TPH data available at DP-65.)
- Maximum Tide Elevation (NOAA Staion 1612340 from 1940 to 2007)
- Minimum Tide Elevation (NOAA Staion 1612340 from 1940 to 2007)

- 20 % NAPL Saturation Contour
- 15 % NAPL Saturation Contour
- 10 % NAPL Saturation Contour
- 5 % NAPL Saturation Contour
- - - Interpreted 0 % NAPL Saturation Contour

Scale Bars in Units of Feet  
Vertical Exaggeration: 15x

Figure 9 - Cross Section C-C'



**Figure 10 - Cross Section D-D'**

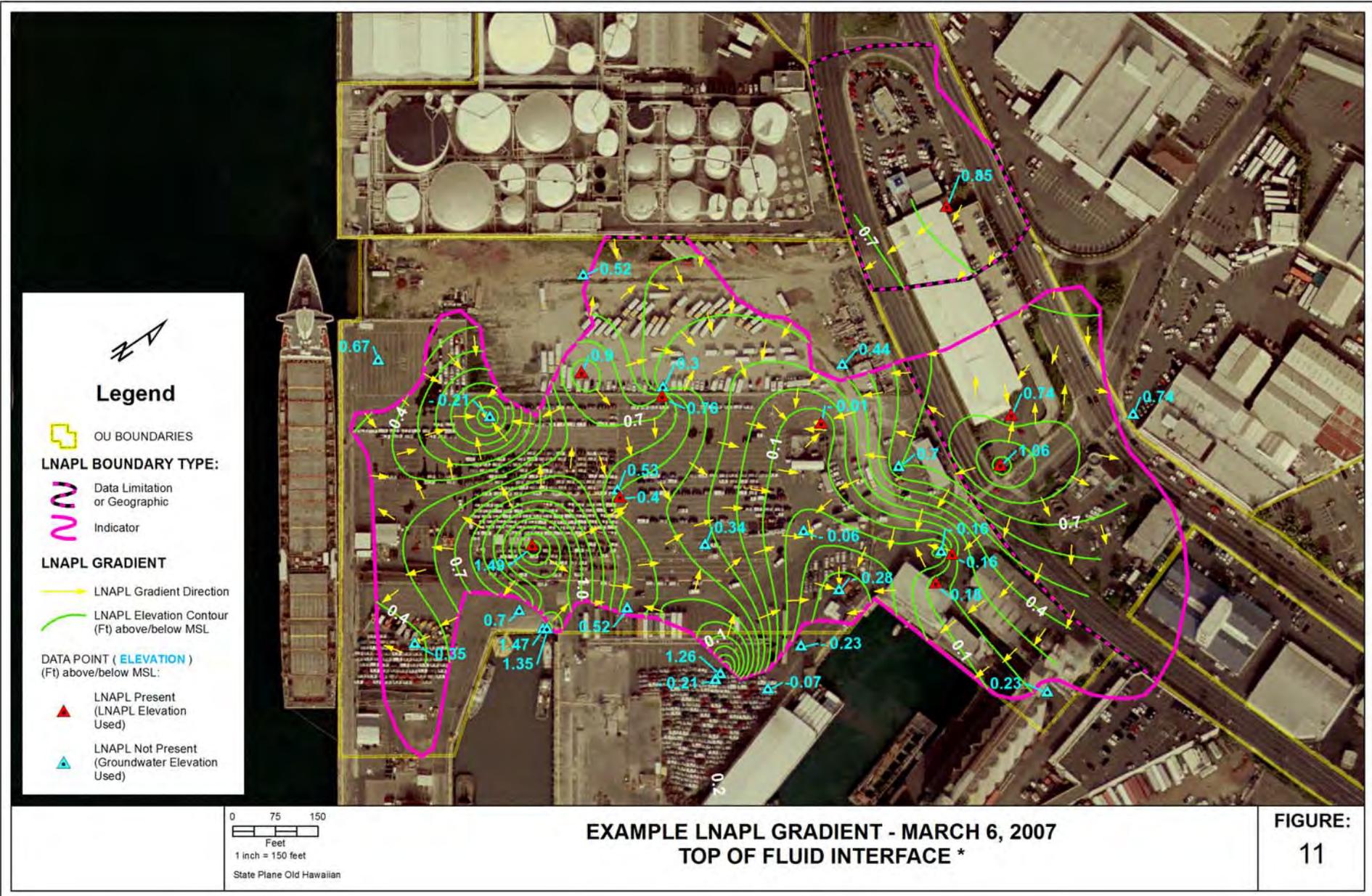
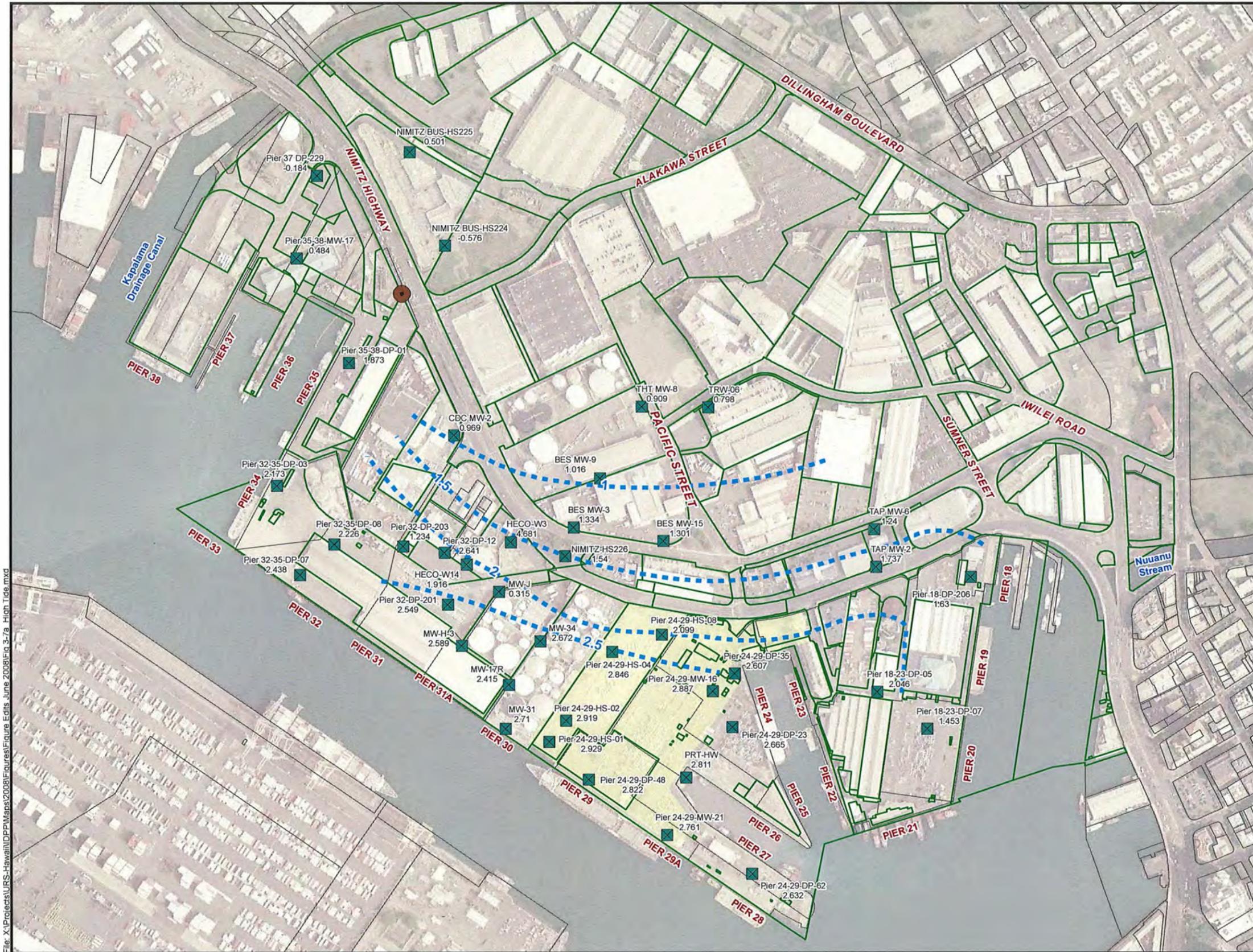


FIGURE:  
11



**LEGEND**

- Monitoring Station
- Hart Street Sewer Station Dewatering Point
- - - GW Elevation Contour
- Parcel

N

0    250    500  
Feet

**Groundwater Elevations  
(feet MLLW) for High Tide  
on May 16, 2003**

Figure 12

File: X:\Projects\URS-Hawaii\NDPP\Maps\2008\Figures\Figure 12 - High Tide.mxd



File: X:\Projects\URS-Hawaii\IDPP\Maps\2008\Figures\Figure Edits June 2008\Fig 3-7b Low Tide.mxd

**LEGEND**

- Monitoring Station
- Hart Street Sewer Station Dewatering Point
- GW Elevation Contour
- Parcel
- Site

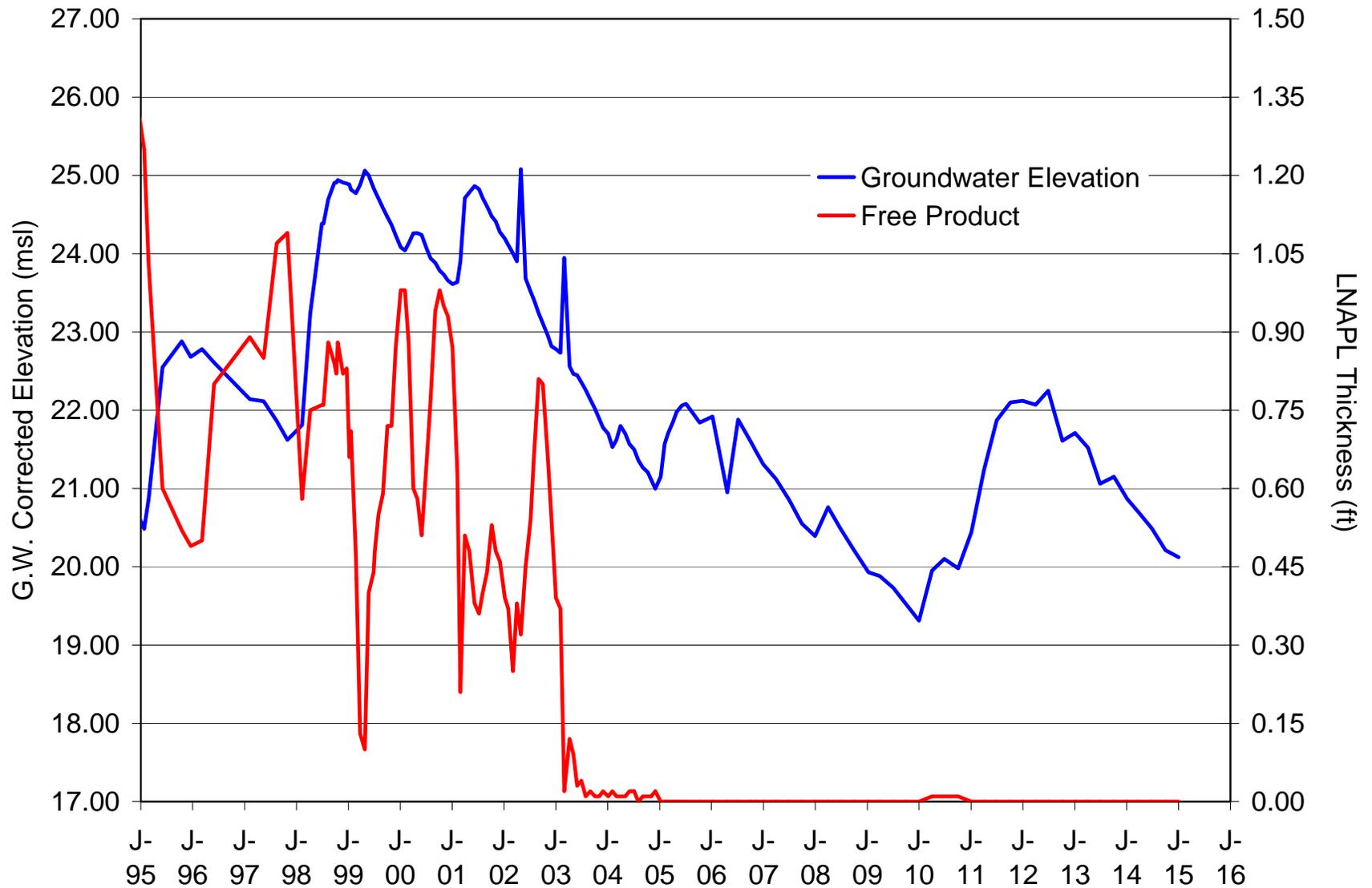
N

0 250 500  
Feet

**Groundwater Elevations  
(feet MLLW) for Low Tide  
on May 16, 2003**

Figure 13

# Figure 14: Periphery Hydrographs with LNAPL



**Legend**

 OU BOUNDARIES

**LNAPL BOUNDARY TYPE:**

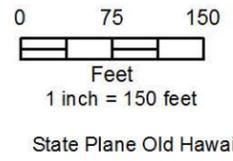
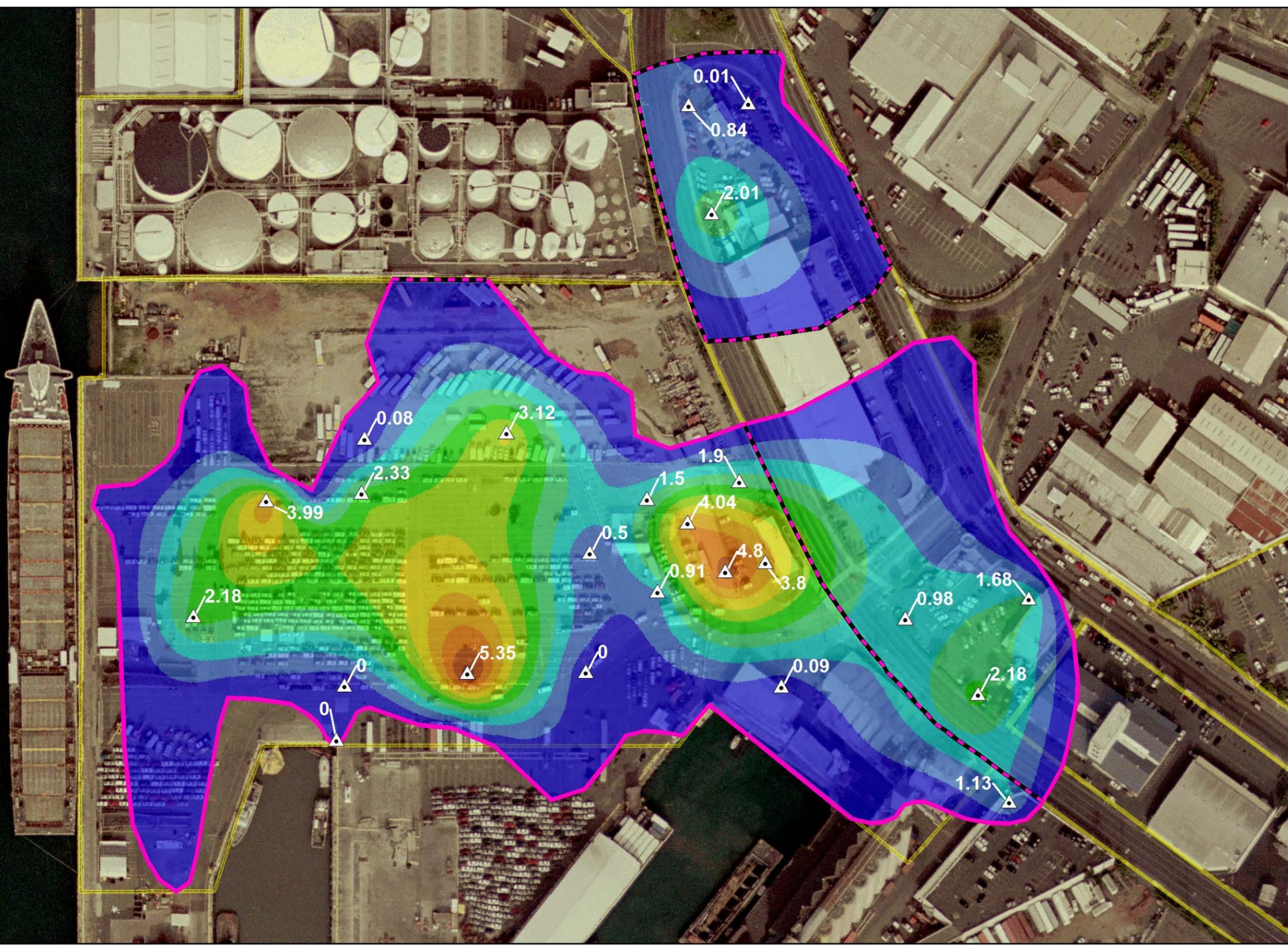
 Data Limitation or Geographic

 Indicator

 DATA POINT

**THICKNESS (Ft):**

	0.00 - 0.50
	0.51 - 1.00
	1.01 - 1.50
	1.51 - 2.00
	2.01 - 2.50
	2.51 - 3.00
	3.01 - 3.50
	3.51 - 4.00
	4.01 - 4.50
	4.51 - 5.00
	5.01 - 5.50



**FIGURE 15**  
**MAXIMUM OBSERVED LNAPL THICKNESS IN MONITORING WELLS - 2002**

**Legend**

 OU BOUNDARIES

**LNAPL BOUNDARY TYPE:**

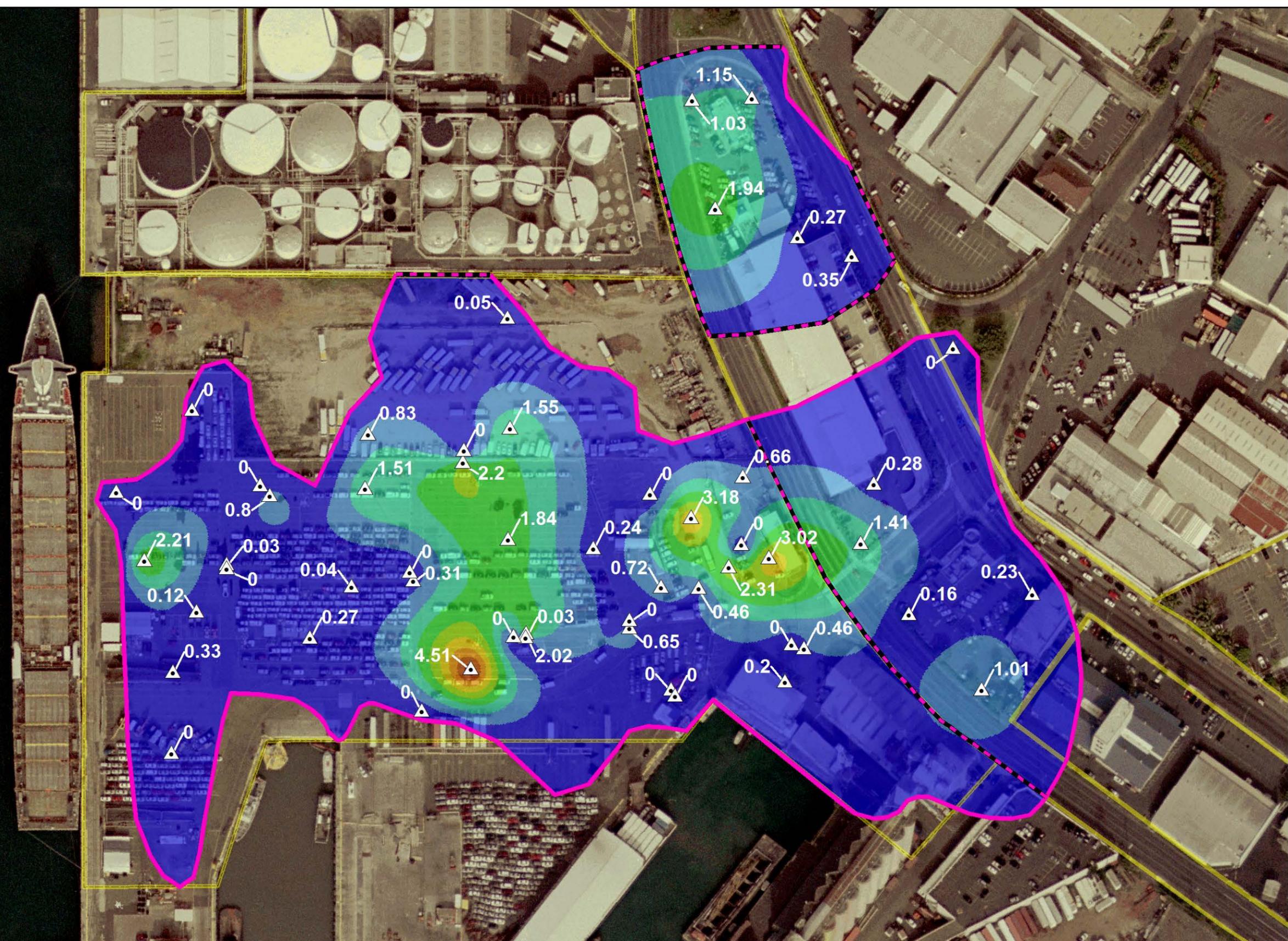
 Data Limitation or Geographic Indicator

 Indicator

 DATA POINT

**THICKNESS (Ft):**

	0.00 - 0.50
	0.51 - 1.00
	1.01 - 1.50
	1.51 - 2.00
	2.01 - 2.50
	2.51 - 3.00
	3.01 - 3.50
	3.51 - 4.00
	4.01 - 4.50



0 75 150  
 Feet  
 1 inch = 150 feet  
 State Plane Old Hawaiian

**FIGURE 16**  
**MAXIMUM OBSERVED LNAPL THICKNESS IN MONITORING WELLS - 2007**



### Legend

OU BOUNDARIES

#### LNAPL BOUNDARY TYPE:

Data Limitation or Geographic

Indicator

#### STORM SYSTEM LINES:

EXISTING LINE

REPAIRED LINE

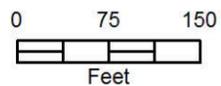
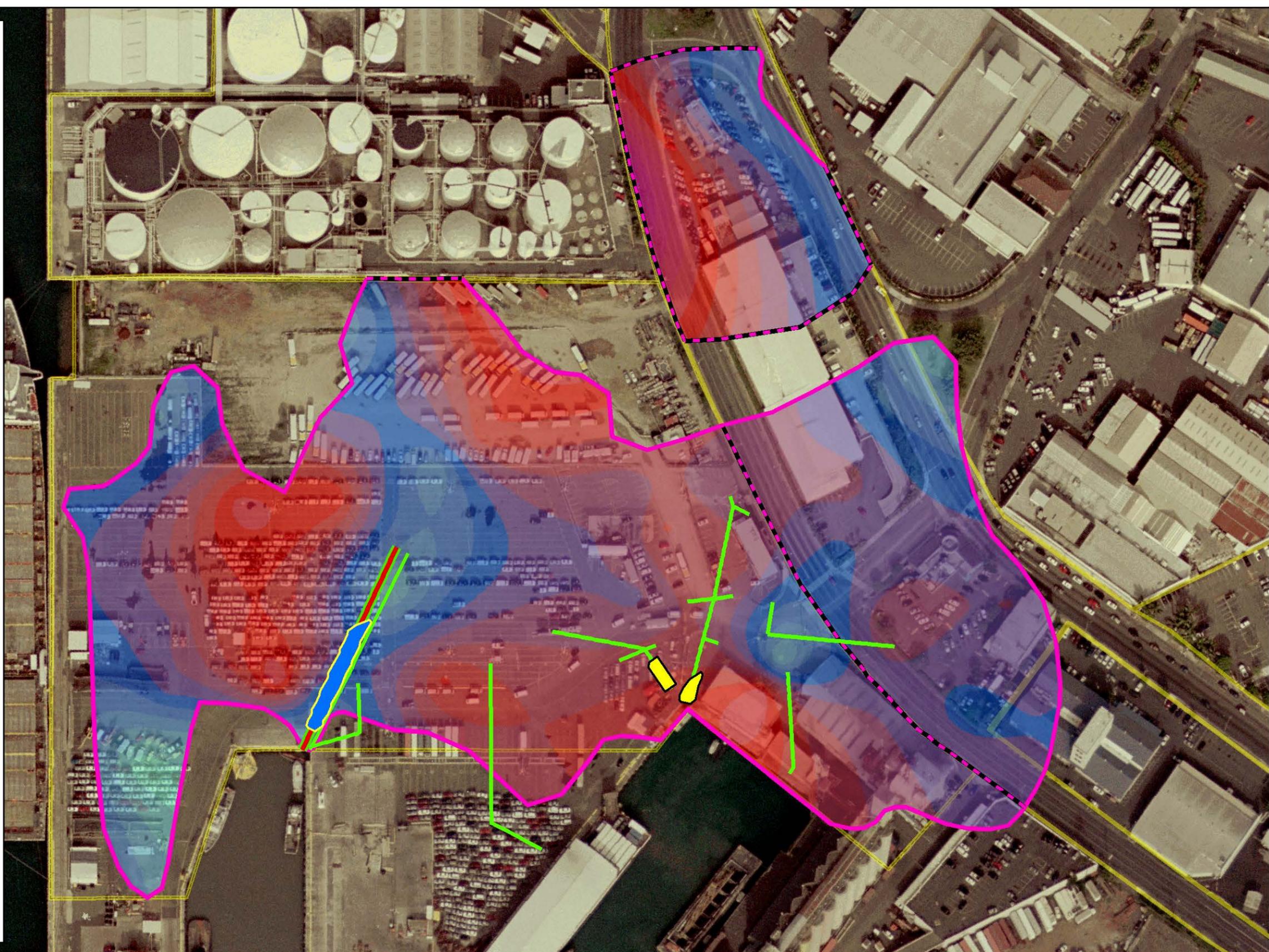
#### STORM LINE / LNAPL INTERSECTION RESULTS:

INTERSECTED DRAIN

REPAIRED DRAIN

#### TOP OF HIGHEST LIQUID INTERFACE (Ft - MSL):

	0.11 - 0.25		2.01 - 2.25
	0.26 - 0.50		2.26 - 2.50
	0.51 - 0.75		2.51 - 2.75
	0.76 - 1.00		2.76 - 3.00
	1.01 - 1.25		3.01 - 3.25
	1.26 - 1.50		3.26 - 3.50
	1.51 - 1.75		3.51 - 3.75
	1.76 - 2.00		3.76 - 4.00



1 inch = 150 feet

State Plane Old Hawaiian

**FIGURE 17**  
**STORM DRAINS AS POTENTIAL PREFERENTIAL PATHWAYS**

Figure 18: Potential Source Identification by Using Groundwater Concentration Ratios

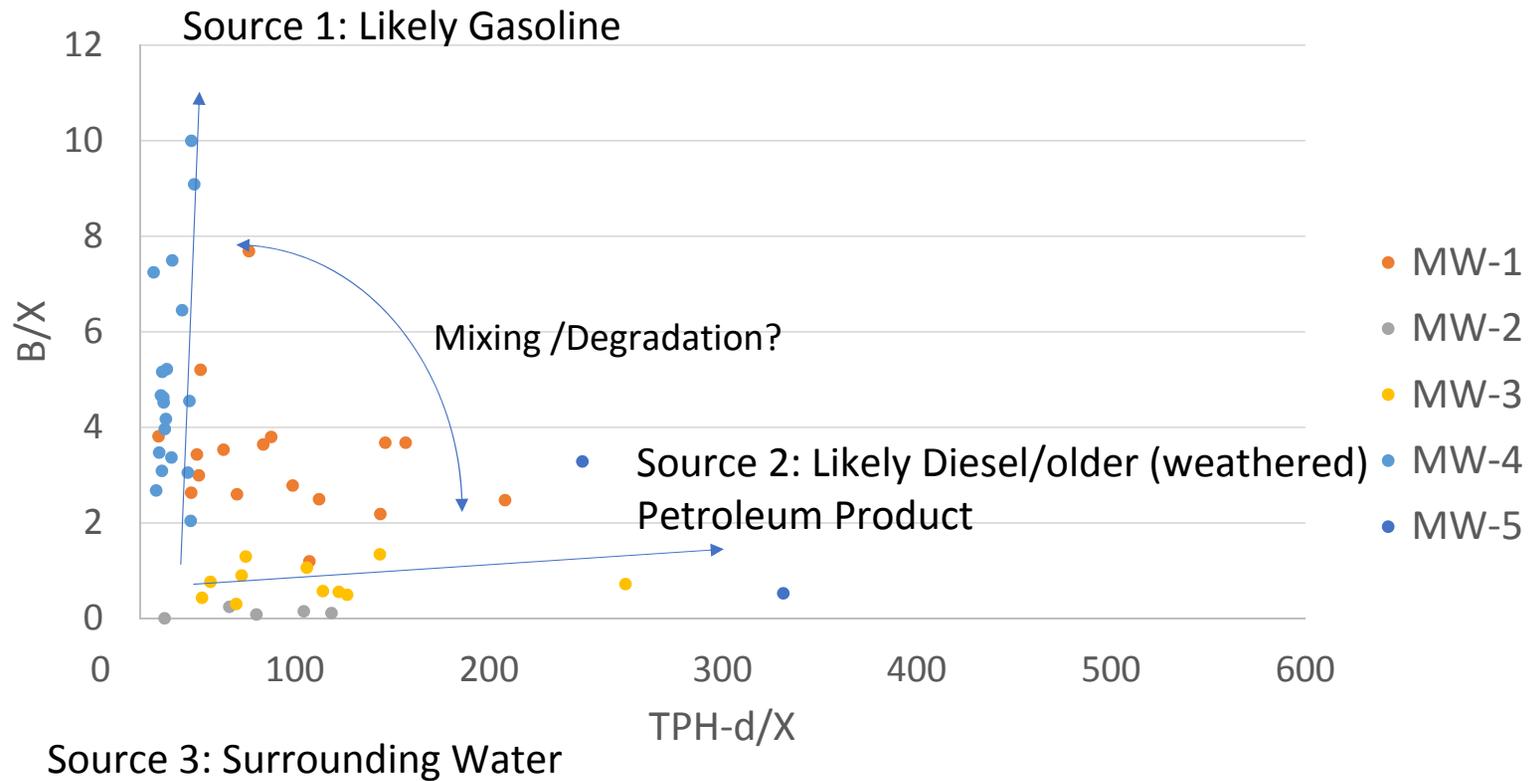


Figure 19: Variability of B/X Ratios With Rising Water Level

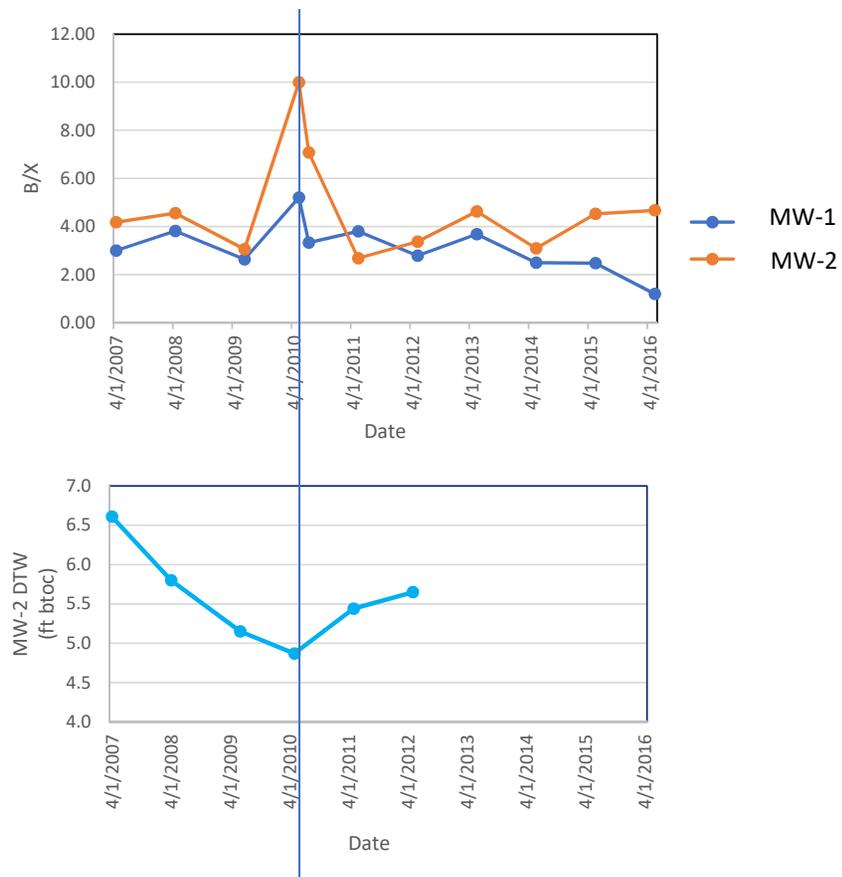
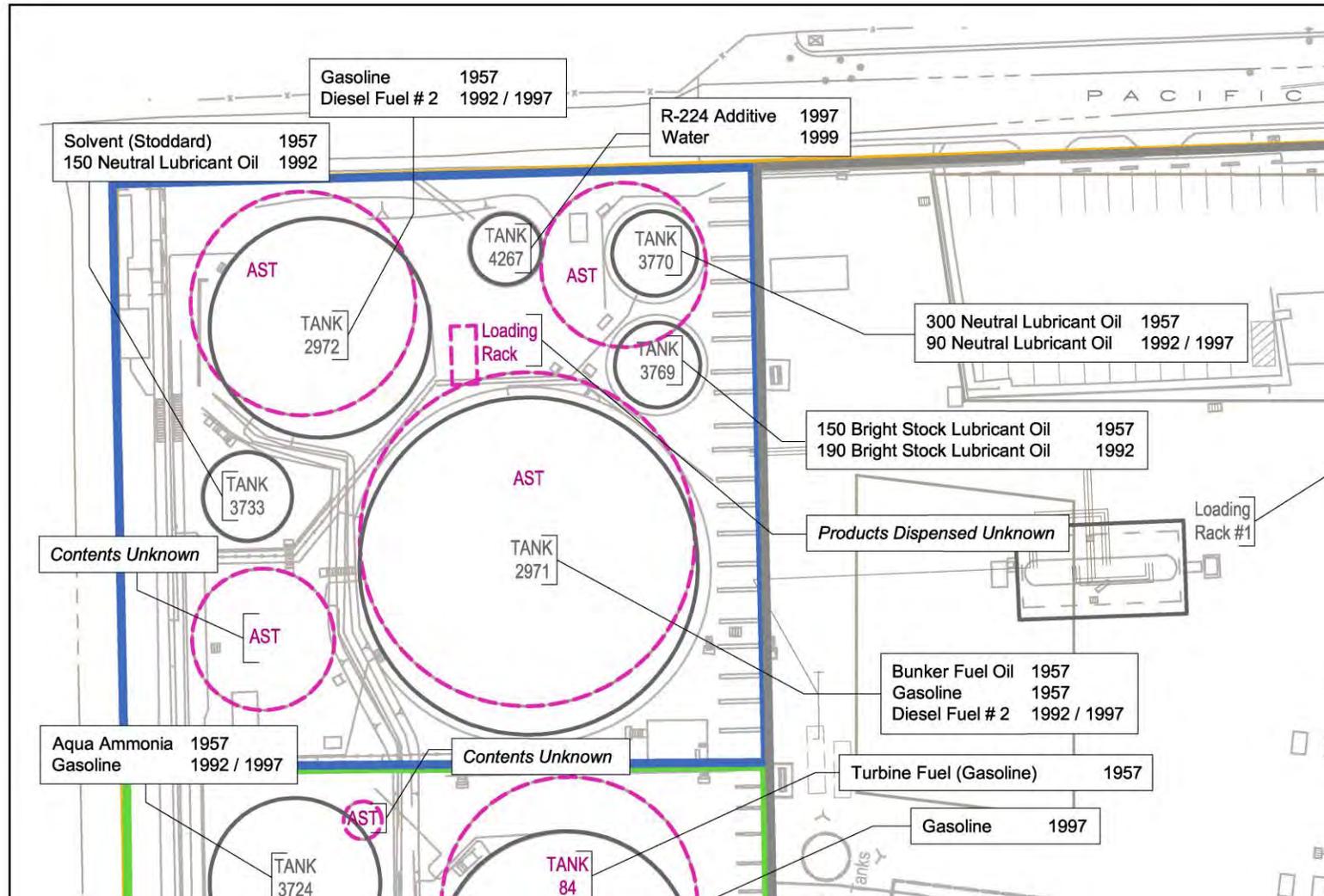


Figure 20: Display of Tank Location, Contents and Year Contents Were Stored





### Legend

OU BOUNDARIES

#### LNAPL BOUNDARY TYPE:

Data Limitation or Geographic

Indicator

#### Weight Percent of 2001 to 2006 LNAPL Sample

Unknowns		Parrarins
Olefins		Isoparrarins
Aromatics		Napthhenics

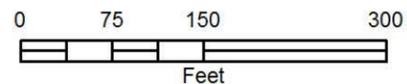
#### Weight Percent of 2001 to 2006 LNAPL Sample

Non-Gasoline Range Organics		Gasoline Range Organics
-----------------------------	--	-------------------------

#### SPECIFIC VOLUME CONTOURS (Gal/Ft<sup>2</sup>):

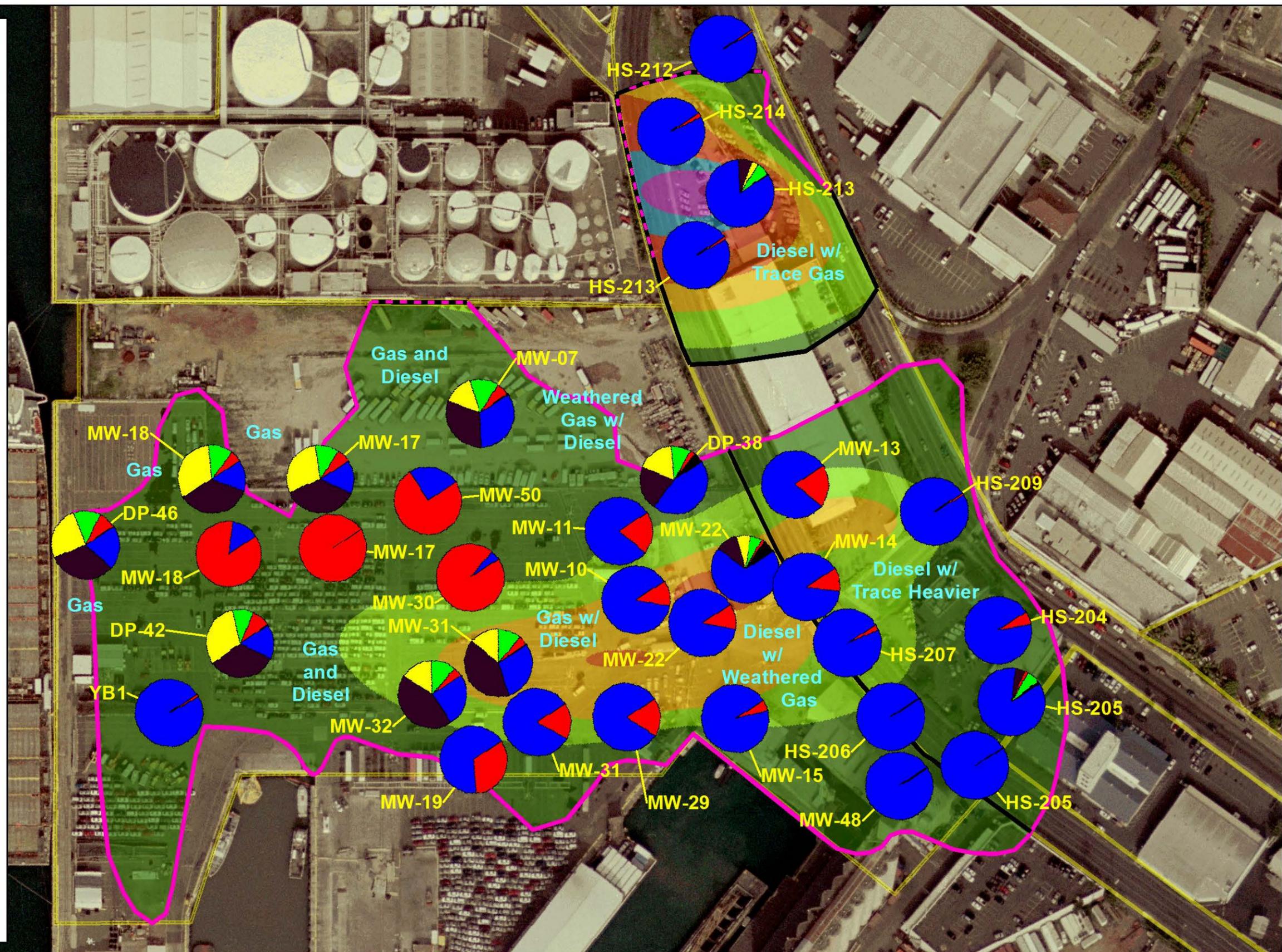
	0.0 - 1.0		4.1 - 5.0
	1.1 - 2.0		5.1 - 6.0
	2.1 - 3.0		6.1 - 7.0
	3.1 - 4.0		7.1 - 8.0

Note: Pie charts are located as close to the sample location as possible.



1 inch = 150 feet

State Plane Old Hawaiian



**FIGURE 21**  
**LNAPL BULK CHEMISTRY**



**Appendix A**  
LNAPL Guide Companion Document



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## 1.0 INTRODUCTION

This LNAPL/Petroleum Guidance Companion Document (Companion Document) pertains to the construction and use of light non-aqueous phase liquid conceptual site models (LCSMs). This Companion Document is a companion to the Hawai'i Department of Health (HDOH) Hazard Evaluation and Emergency Response (HEER) Office Technical Guidance Manual (TGM) Section 9.3, which was created to assist users in constructing the LCSM for LNAPL releases to the subsurface. This Companion Document is not technically all-inclusive, as the many aspects of LNAPL release and migration mechanics are beyond the scope of a single document. More in-depth information and reading can be found in the attached Bibliography of relevant technical materials.

### 1.1 REGULATORY FRAMEWORK

As outlined in Section 1.0 of the TGM, the HEER Office has the responsibility and legal authority under Chapter 128D, HRS to respond to releases, threats of releases, or discoveries of Hazardous substances, including oil, that presents a substantial endangerment to public health or the environment. The HEER Office is also involved in oil spill prevention planning, preparedness and response activities as required under the federal Oil Pollution Act (OPA) of 1990. In general, the HEER Office regulates historic releases and is not involved in the regulation of active petroleum facilities, which are regulated by the Underground Storage Tank (UST) Section of the HDOH Solid and Hazardous Waste Branch (SHWB). However, since the UST Section does not regulate above ground storage tanks and underground tanks less than 110 gallons, fuel terminals, and releases from tanks and hoists fall under the responsibility of the HEER office. LNAPL is an inclusive term for industrial oils and fuels lighter than water (light non-aqueous phase liquid).

### 1.2 DOCUMENT SCOPE

This Companion Document is intended to assist users in developing a technically sound LCSM upon which site mitigation decisions can be founded. Standard guidelines for development of a conceptual site model (CSM) are presented in Section 3.3 of the TGM. The LCSM differs from a standard CSM in that the specifics of multiphase mechanics are explicitly developed. This is necessary for any LNAPL site because those mechanics control the transport, risk and cleanup of both the LNAPL and the associated dissolved- and vapor-phase plumes. This Companion Document is the foundation, source, and companion to the LNAPL section of the TGM and provides references to further reading and detailed descriptions. A Glossary of common technical terms is included with this document.

One goal of this Companion Document is to expand the use of commonly collected site data in LCSM development that are often underutilized, and to refrain from additional data collection unless warranted. Although modeling is often helpful in understanding LNAPL mechanics, the HEER Office encourages thoughtful data interpretation as the first-line of a technical approach to LCSM development. Modeling, particularly the use of heuristic models, can often lead to incorrect conclusions about the potential risk and cleanup of LNAPL plumes. When modeling is used to assist in LCSM development, the analysis and results should reasonably bracket actual subsurface conditions, and the major assumptions and limitations of the model utilized should be described. Procedures and

lines of evidence acceptable to the HEER office in LNAPL development and release response are outlined below.

### 1.3 TIERED APPROACH TO LNAPL SITE EVALUATION IN HAWAII

This Companion Document is structured for easy implementation and resulting mitigation decisions. While grounded in multiphase and contaminant transport mechanics, the detailed technical aspects will be handled primarily by reference to materials outside this document. A brief introduction to these mechanics will be discussed herein, along with some key implications to release site management in Hawai'i and the important factors controlling release genesis and cleanup. This will set the context for a tiered decision process for evaluating existing site data and improving the associated CSMs where necessary to ultimately arrive at site mitigation decisions leading to closure.

The LCSM is the foundation of site mitigation decisions. The complexity and robustness of the LCSM will depend on the conditions and the potential risks posed by the subject releases(s). Figure 1 is a schematic of factors that affect the LCSM complexity and categorization into different Tiers. Sites with very low probable risk (Tier I Sites) are likely to require less data collection, interpretation, and scrutiny than sites with a high probable risk (Tier III Sites). For example, a small release from a service station that does not overlie drinking water and is far from other receptors (Tier I) would typically require less interpretive effort than a large petroleum facility with multiple large volume, potentially mobile releases situated near potential receptors. The former would be deemed a Tier I site in terms of risk and complexity, whereas the latter would be deemed a Tier II or III release site (depending on specifics and potential risks). With higher Tiers, complexity is increased, Figure 2 is a generic LCSM graphic that shows a few relevant components.

### 1.4 WHAT IS AN LCSM?

The LCSM is the cornerstone of site mitigation decisions. The complexity of the LCSM will depend on site release conditions and the potential risks posed. Because LNAPL is the concentrated source of impacts in its own phase, as well as derivative phases (generally dissolved- and vapor-phases), it is the focus of an LCSM. Figure 1 is a schematic of factors that affect that LCSM complexity and depth. Figure 2 is a generic Tier I LCSM supporting graphic that includes a few example LCSM components.

The LCSM is similar to a standard CSM. It is a description of the context, setting, distribution, transport and receptors of any given LNAPL release, with a focus on the LNAPL and associated multiphase facets. For our purposes here, LNAPL includes both that observable in monitoring wells (free-phase or mobile-phase) and the residual component (immobile and held by capillary forces in the soil); i.e., an LCSM may be warranted even if floating LNAPL is not present. The goal of the LCSM is to describe the nature, geometry, and setting of the LNAPL and daughter-plumes (dissolved- and/or vapor phases) in sufficient detail to adequately address questions regarding potential risk, future threats, longevity, and amenability to remedial options.

The LCSM is typically a combination of descriptive and pictorial representations of plume conditions past, present, and future. Like any CSM, the purpose is to package the suite of knowledge, data, interpretations, and assessments into a comprehensive story to assist in evaluating potential risks and appropriate mitigation actions. The LCSM development process will often identify data/knowledge gaps that can be addressed, if of sufficient importance. As new knowledge is gained, the LCSM should be updated to incorporate this new understanding.

The basic components of an LCSM include: 1) LNAPL characteristics; 2) LNAPL plume delineation; 3) Assessing LNAPL Mobility; 4) LNAPL release conditions; 5) Hydrogeologic conditions; 6) Hawai'i specific considerations. The complexity of each component will depend on the probability of environmental risks combined with site specific cleanup requirements. The tiered approach for the LCSM development is flexible and site specific, but as a general guideline, the tiers typically include the following:

Tier I: Uses existing standard site data to define the LNAPL and daughter plume extent in three-dimensions (3-D), hydrogeologic setting, potential for plume mobility and migration, receptors and risk context.

Tier II: Combines existing site data with more advanced data collection and/or evaluations to further refine one or more of the elements of the LCSM. Depending on which LCSM element is lacking, this might include more detailed 3-dimensional characterization work using continuous coring, geophysical, or other techniques. Tier II data often includes forensic chemistry analyses to better determine LNAPL release sources and characteristics. Heuristic modeling may be informative to the Tier II LCSM as long as the results reasonably reflect measured subsurface conditions and the underlying assumptions and limitations are applicable.

Tier III: Combines the facets of the Tier I/2 evaluations, and typically adds more rigorous spatial and temporal analyses of plume conditions and risk. Tier III evaluations may include more advanced data collection and may include modeling evaluations using robust transient methods. Modeling is typically used when questions of future plume conditions and associated risk become important. Again, the model selected and modeling approaches must be consistent with underlying site conditions. For instance, it would be generally inappropriate to use a porous-media model for fractured flow conditions, just as it would be to use an equilibrium model for a transient system.

## 2.0 SUMMARY OF LNAPL MECHANICS

This brief discussion on LNAPL release principles provides context for the genesis and mitigation of those releases. The terms “oil” and “LNAPL” will be used interchangeably throughout this Companion Document; “oil” is the classic terminology for the non-wetting liquid and is commonly used in technical literature. These principles guide and assist in the interpretations of site data for consideration of LNAPL distribution, migration, mitigation, recoverability, and other aspects at issue for these types of releases. In simple terms, a multiphase environment is one in which water, oil and/or vapor, which are immiscible phases, vie for pore-space as a function of the capillary pressure between the phases and the physical nature of the pore space itself. After the wetting phase (i.e., water and soluble constituents), the non-wetting phase (such as oil or air) occupies the larger voids of the overall pore- and can be displaced by the wetting phase under certain conditions. Water is usually the wetting phase and is naturally present long before the introduction of LNAPL, the presence of which changes the multiphase conditions (initially air/water, subsequently air/water, oil/water, oil/vapor - the multiphase couplets). The wetting phase adheres most closely to the pore walls and is not as easily displaced from the small voids in the pore space.

LNAPL flow and stabilization (mobility/stability & volume) can be understood through the physics controlling the movement of one fluid phase in the presence of other phases (multiphase flow). Multiphase physics account for the hydraulic interactions and movement of multiple fluids in the soil pore space, typically water, vapor, and LNAPL. These physics control the genesis of LNAPL plumes following releases to the subsurface. Ignoring compositional reactions, multiphase mechanics are governed by the Continuity Equation for mass conservation (Equation 1), which describes the mass movement of any phase in any direction for a non-deforming coordinate system (Huyakorn et al., 1994; Panday et al., 1994). Simplified representations of these physics are available in various LNAPL evaluation tools developed by the American Petroleum Institute (API), United States Environmental Protection Agency (EPA) and others (see resource list above).

$$\frac{\delta}{\delta \chi_i} \left[ k_{ij} k_{rp} \frac{\rho_p}{\mu_p} \frac{\delta \Phi}{\delta \chi_i} \right] = \frac{\delta}{\delta t} (\theta \rho_p S_p) - M_p \quad (\text{Equation 1})$$

Where: “M” is the differential operator,  $\chi_i$  indicates the Cartesian direction of the 3-dimensional differential equation;  $k_{ij}$  is the intrinsic soil permeability,  $k_{rp}$  is the relative permeability to phase “p”, subscript “p” refers to the fluid phase of interest,  $\Phi$  is the fluid potential ( $\mathbf{M}\Phi/\mathbf{M}\chi_i$  is the fluid potential gradient), “t” is time,  $\theta$  is soil porosity,  $\rho_p$  is the density of phase “p”,  $S_p$  is the phase saturation, and  $M_p$  is a mass source/sink term.

Despite the complexity of the multiphase continuity equation, the principles it represents are straightforward. Phase movement (water, LNAPL, or vapor) in any direction (represented by the left side of the equation) is controlled by the fluid and soil properties and the gradient in that phase at any point in time and space. Net phase movement into or out of an elemental volume must be equaled by a coincident change in mass within that volume (the right side of the equation). When

either the phase conductivity or the phase gradient is zero, there is no phase movement or mobility. The fluid potential  $\Phi$  includes a gravity term, and for LNAPL, is driven by the conditions of the LNAPL release, overprinted to varying degrees by the water table gradient.

Further, based on these principles, one can make some simplifying assumptions from which free-phase (mobile-phase) saturations in the ground can be related to observed LNAPL thicknesses in wells; those assumptions are called multiphase vertical equilibrium (VEQ) mechanics (e.g., Parker, 1989; Farr et al., 1990). The mobile LNAPL and water saturations are determined by the fluid levels (pressures) in monitoring wells and the capillary properties of the soil and the oil in the free product interval. These VEQ estimates pertain only to the mobile LNAPL, as residual product does not flow into a monitoring well. The VEQ model is discussed in more detail subsequently.

The early stages of the release are highly transient and LNAPL will migrate rapidly due to the underlying nonlinear physics. A generalized LNAPL plume, superimposed on a groundwater gradient, would develop through time as shown in the time series sequence on Figure 3. With time, the LNAPL gradient dissipates and the mass redistributes laterally, depleting a fraction of the concentrated central mass that was present during the early stages of the release. LNAPL saturation, volume and recoverability generally remain greatest in the central release area and lesser in distal areas, but they are also affected by heterogeneity. In some cases, the distal areas are a concern because of potential risks to receptors through mobile-phase migration.

Over time a finite LNAPL release will slow exponentially, eventually coming to static equilibrium with the prevailing field conditions. There are five key mechanisms, given below, that explains this expected stabilization through time, each of which is also affected by heterogeneity in any of the relevant controlling parameters.

1. After the initial release, the source area LNAPL gradients and well thicknesses both diminish through time (presuming the source has been eliminated), as the gradients created by the release cannot be sustained without newer releases. The volume in the mobile zone is proportional to the thickness in the well and the soil/oil capillary properties. While the LNAPL well thicknesses in the source area are dissipating, a migrating plume will exhibit new arrivals at peripheral monitoring well locations that did not previously exhibit floating product.
2. LNAPL will often flow in all compass directions around a release area, with some influence from the ambient groundwater gradient. During the early stages of an LNAPL release, LNAPL does not typically follow the groundwater gradient (it follows the radial LNAPL gradient). Many LNAPL plumes retain the propensity for radial flow for long periods.
3. Most porous materials have a pore entry pressure, and non-wetting fluids (LNAPL and air in most cases) cannot intrude without a sufficient gradient in that phase to overcome the entry pressure. As the gradient diminishes, further plume migration is impeded by this entry pressure at the lateral boundaries.

4. The LNAPL effective conductivity diminishes through time as the finite volume of oil is distributed over a larger volume of aquifer material. As this occurs, the overall LNAPL saturation decreases as a function of spreading and the relative permeability toward oil decreases exponentially. This is accentuated by water table fluctuations, where present, that can redistribute LNAPL over larger volumes of aquifer/soil materials.
5. Soil has a capacity to hold oil in a residual state (i.e., residual LNAPL is immobile). This means that a finite LNAPL release will theoretically be retained as residual at some maximum spreading distance. In practice this maximum spreading distance is not generally reached because of the other facets of stabilization. A plume where all the LNAPL has moved into the residual state would no longer exhibit mobile LNAPL in observation wells.
6. Natural mass losses from the LNAPL reduce and weather the mass in-place over time, as do engineered recovery actions. These mass losses will have a tendency to reduce overall LNAPL saturation in the subsurface, in turn reducing the potential mobility as well as changing the LNAPL chemistry over time through weathering processes.

Based on these principles, finite LNAPL plumes come to field equilibrium in relatively short time frames. Based on general multiphase modeling for a wide range of conditions, a finite LNAPL release should stabilize and cease to move in approximately three to eight years (e.g., Figure 4), with small releases stabilizing more quickly than larger releases. Although this range is general, the physics controlling plume movement clearly indicate that LNAPL will stabilize after a relatively short period of spreading. Ongoing or new releases obviously change this scenario. As discussed below, dissolved-phase and vapor-phase daughter plumes also develop over a finite time frame. However, the persistence of plumes (as opposed to equilibration time) are typically much longer for both the LNAPL and daughter plumes.

This time dependency of the LNAPL plume genesis is critical in the development of the LCSM. For instance, probabilities suggest that old LNAPL plumes are geographically stable. “Old” can be determined by known release timing, chemical signatures, and other indicators that will be discussed subsequently. Similarly, the aspects and timing that stabilize LNAPL plumes cause them to be less recoverable by hydraulic means, since recovery is just flow under an induced gradient. Old LNAPL plumes are generally unrecoverable in any significant fraction relative to the total mass in-place. That recovery could have benefits for further plume stabilization, but does little in the way of chemical source reduction because the majority of mass will remain to partition into the environment, often for long time frames depending on the chemicals of concern (CoC).

## 2.1 PARAMETERS CONTROLLING LNAPL TRANSPORT AND DISTRIBUTION

As can be observed from Equation 1 above, we need a way to quantify (rigorously or conceptually) the various factors controlling LNAPL migration and distribution. How does one define relative permeability, for instance, or the degree of pore saturation of each phase? How are those things and others related? And most important, what does any of that tell us about LNAPL plume mobility, potential risk, and implications to remediation?

This overview of physical parameters will focus on parameters with the greatest sensitivity to LNAPL transport and distribution in the subsurface to assist in providing a solid framework for the LCSM. The API Interactive LNAPL Guide has a relatively thorough discussion of these and the wider range of controlling parameters, along with references to that development. Appendix A of this Companion Document contains additional introductory discussion of the more sensitive parameters. The site-specific examples of LCSM building will help show how these parameters and other factors fit into the evaluation process. Table 1 in the Appendices lists common LCSM parameters/factors, their sensitivity, and how one might define those values.

### 2.1.1 Capillary Properties

The capillary properties of soil and the LNAPL are probably the single-most important set of parametric controls because of their nonlinearity and sensitivity in many multiphase relationships. For the pristine water/air system (i.e., before an LNAPL release), the distribution of water as a function of the pore network and capillary pressure is represented by a characteristic curve. Figure 5 shows a family of capillary characteristic curves for different soil types, varying from fine- to coarse-grained.

Capillary properties control the relative saturations of each phase (air, water, and LNAPL) in the presence of the other and dependent on the capillary pressures between the phases. Basically, the greater the capillary pressure, the greater the LNAPL saturation. For a given pressure, LNAPL saturations will be greater in coarse-grained materials than in fine-grained. Figure 6 shows the theoretical LNAPL distribution for several soil types at an assumed well thickness of 1 m (~3.28-ft). As observed, there is significant variability in mass for the same equilibrated LNAPL thickness, and as discussed subsequently, corresponding difference in mobility, risk, longevity and amenability to cleanup. For example, the LNAPL mass per square meter is much larger (by an order of magnitude) in coarse sand (56 kg) than in silty sand (3 kg). These estimates are derived through the VEQ model that will be discussed in Chapter 3. This also means the plume morphology in different soils will be strongly affected by these properties; typically thinner and wider plumes in coarse materials versus thicker and less distant in fine-grained materials.

Soil capillary properties can be derived from laboratory testing data that are fit to one or more capillary models. They may also be derived from literature values, as appropriate, typically a reasonable starting point for estimates of LNAPL saturation, mobility and recoverability. See the provided references for a more complete discussion of capillarity and parameter determinations.

### 2.1.2 Standard Petrophysical Properties

Standard petrophysical properties refer to those that are common to both standard hydrogeologic applications and multiphase mechanics. These include intrinsic permeability, hydraulic conductivity, bulk and grain density, grain-size distribution, and porosity. Each of these has a place and effect in multiphase mechanics that is analogous to standard hydrogeologic practice and they will not be discussed further herein except within their subsequent application to LNAPL transport,

cleanup and risk. The API Interactive LNAPL Guide has a good discussion of these properties and their effects in multiphase mechanics, as do others of the external resources provide earlier in this Companion Document.

### 2.1.3 Relative Permeability and Effective Hydraulic Conductivity

As already noted, when multiple fluids share the pore space, the ability of each to move is impeded by the others. Relative permeability is a scalar (0 - 1) that accounts for the reduction in flow capacity of each phase in the presence of other phases. The relative permeability is nonlinearly related to the relevant phase saturations, where decreasing saturations imply even more dramatic decreases in relative permeability (and mobility). That nonlinearity is critical in the ability of LNAPL to move or be recovered (or not) in the presence of water in the pore space. In general, the lower the phase saturation, the smaller the relative permeability to that phase, eventually reaching some *de minimis* ability to migrate. While there is no absolute value for *de minimis* mobility, a common threshold is an effective conductivity of  $10^{-6}$  cm/sec, the value for a Class I Landfill Liner.

The effective conductivity is the product of the relative permeability multiplied by the saturated hydraulic conductivity of each phase. The effective phase conductivity and transmissivity are field-scale parameters that are key controls over LNAPL mobility.

LNAPL slug tests (a.k.a., baildown tests) and pumping tests can be used to estimate the in situ LNAPL transmissivity under the hydrogeologic conditions of testing (i.e., see Figure 7). However, because the LNAPL distribution is non-uniform (recall Figure 6), the associated average hydraulic conductivity derived from transmissivity is non-conservative because it mutes the zones of highest saturations and effective conductivity. LNAPL conductivity can also be estimated from petrophysical testing, but the scale of sampling often causes this approach to underestimate the effective conductivity. In short, one must keep the multiphase features in mind when evaluating LNAPL field or lab-scale data to estimate the effective conductivity of the LNAPL.

### 2.1.4 Residual and Effective Saturation

Residual saturation toward any liquid phase (water or oil) is the threshold value below which that fluid is retained as immobile by soil capillary forces and entrapment. There are two types of residual saturation; 2-phase residual is where oil and water are present below the water table with negligible vapor-phase content, and 3-phase residual in the vadose zone. While this is common to the definitions in our industry, it should be noted that 2-phase residual with respect to LNAPL is typically comprising two parts, true residual and an additional fraction that is occluded with the water-wet environment. When the water table falls, that occluded fraction may move or drain, and this explains the often observed increase in mobile-phase product thickness in monitoring wells when water tables fall (e.g., Figure 7). As such, many published or lab-measured 2-phase LNAPL residuals are not necessarily reflective of immobility under all conditions, but only under those specific conditions tested. One must interpret these data within the site hydrogeologic context to assess whether an implication of immobility is valid. For instance, if site specific LNAPL saturations are below a 2- phase residual threshold, but there has been historic free product observed at low water table stands,

then true 3-phase residual values would be more applicable, and the 2-phase residuals valid only for a submerged condition.

LNAPL remobilization under falling water tables is the transient occurrence under which previously immobile LNAPL becomes potentially mobile. Careful evaluation of fluid level gauging and analytic chemistry data can assist in elucidating whether increases in well thickness due to falling water tables are merely vertical redistribution or indicates lateral plume migration. Actual migration may be indicated by new occurrences of LNAPL and dissolved-phase impacts at locations that were previously unimpacted.

Last, while more rare, it is possible for oil to be trapped under confined conditions where the opposite well responses can occur; i.e., increased LNAPL thickness with increased hydraulic head (e.g., height of the piezometric water level indicating higher water pressure).

The language and estimates of multiphase mechanics are typically given in terms of fluid saturations, or the fraction of the pore space occupied by each phase. Saturation measurements are not always available in site specific data, but soil TPH values often are. While not explicitly a “parameter,” it is useful to observe that TPH can be converted to saturation fairly easily using the equation below, where  $D$  is the density of oil and field soil ( $\rho_o$  and  $\rho_{fb}$  subscripts) and  $\theta_t$  is porosity. There are a few considerations and limitations to this estimate. First, if the TPH analysis did not include the full spectrum of carbon ranges actually present, then the results will be artificially low. Second, labs typically utilize a field sub-sample that contains soil, pore water, and LNAPL. So the mass of all those components makeup the field bulk density (i.e., it is not a dry weight). Third, if LNAPL saturations are high enough in situ, then liquid drainage can occur on sample retrieval from the borehole and those losses will not be reflected in the TPH results. In short, while this conversion estimate can be useful, it typically underestimates the LNAPL saturation.

$$S = \frac{TPH (mg / kg)}{\rho_o} \cdot \frac{\rho_{fb}}{\rho_o} \cdot \theta^{-1} \cdot 10^{-6}$$

### 2.1.5 Fluid Properties

Several fluid properties are important to LNAPL transport and cleanup. These include viscosity, interfacial tensions (IFT), and density. Of these, the IFT is most sensitive as the parameter is used in capillary calculations and has a nonlinear effect. Viscosity can vary widely between LNAPL types, with gasoline having the lowest viscosity of common fuels, and therefore the highest innate mobility. Density does not vary widely, but does have an effect on estimates of capillary pressures and a minor effect on mobility. Figure 8 shows the generalized contrasts in LNAPL mobility as a function of viscosity and density of selected products. Note that the variability in situ is much larger since that is a function of both the fluid properties and the relative permeability, in turn a function of the saturations.

## 2.2 DISSOLVED AND VAPOR-PHASE PLUME DEVELOPMENT

Virtually all persistent dissolved- and/or vapor-phase petroleum daughter plumes are sourced from mobile or residual LNAPL in the pore-space. It is important to recognize that residual LNAPL is a potentially strong source of daughter-phase impacts even if LNAPL has never been observed as free product. This is common in older plumes where the original LNAPL release has entered the residual phase over time, but that residual material still provides a source term for dissolved- and vapor-phase impacts. As will be discussed subsequently, this is why the residual from either ambient or remediation conditions determines the plume longevity. Generally (and all other things being equal) a large residual mass will persist for a much longer time frame than a small mass.

In typical LNAPL releases, a central area or areas of high dissolved- or vapor-phase concentrations will be present that tend to remain in the same vicinity corresponding to release source areas. Exceptions are of course possible for highly transportable and soluble compounds, like fuel oxygenates that commonly detach from source areas (e.g., Wilson et. al, 20XX), and in unusual hydrogeologic setting.

Most petroleum fuels and crudes are composed of hundreds to thousands of distinct chemical compounds. Each compound has distinct properties that affect how it dissolves, volatilizes, and is transported in the subsurface environment. In general, lighter molecular weight compounds have greater solubility and volatility than heavier compounds and are transported more readily. As a result, those compounds can be fractionated (partly decoupled) from each other in water and residual soil. For instance, MTBE will travel faster and arrive at sentry locations before benzene, which in turn may migrate and arrive sooner than a heavier compound like naphthalene. As an LNAPL release continuously partitions chemicals to soil, groundwater, and vapor, the composition of the source changes and in turn that affects the remaining partitioning. In other words, chemical partitioning is an ever-changing process as the LNAPL release ages under environmental exposures.

As soon as the LNAPL enters the subsurface, these partitioning and transport mechanisms begin to form daughter phases. In cases where the LNAPL release is laterally mobile/migrating following the release, it may outpace the dissolved-phase plume. But as the LNAPL migration inevitably slows (for a finite release), the dissolved-phase develops a halo around the LNAPL source. Figure 9 shows an example of a sentry well in a dynamic release situation where initially dissolved-phase concentrations are non-detect, arriving at the sentry well in increasing concentrations over 12 months and culminating with the arrival of mobile phase LNAPL.

From a theoretical point of view, biodegradable dissolved- and vapor-phase plumes reach their dynamic equilibrium around the LNAPL source within approximately 1 to 5 years, depending on the various fate and transport controls over those daughter plumes (and of course there are exceptions). Figure 10 shows the estimated downgradient transport and development of dissolved-phase plumes for gasoline constituents under a wide range of conditions. As seen, and consistent with the findings of gasoline plume length studies, dissolved-phase plumes develop over the short-term and come to equilibrium some distance from the source, before contracting in late-time

as that source depletes. One can use semi-analytic transport models, like that found in the API Interactive LNAPL Guide, or numerical models to make such estimates on a site-specific basis (again, more on modeling subsequently).

### 2.2.1 Multicomponent Chemical Processes

Multicomponent chemical processes refer to the complex relationships between chemical fluxes, transport, longevity and risk when addressing petroleum LNAPLs composed of many different chemical species. When a single chemical like benzene, is present, the equilibrated water- and vapor-phase concentrations are simply those in published literature (~ 1,780 mg/l in water and 324 mg/l in vapor). For as long as the source remains, these will be the approximate concentrations in water and vapor within the source/release zone.

However, in a multicomponent fuel situation, like gasoline, benzene is only one of many compounds of concern. In this case, the solubility and volatility are proportional to both its pure-phase properties and its molar fraction in the fuel (see reference materials for further discussion). This causes a sequential partitioning of various chemicals, with lighter and more soluble/volatile compounds dominant in the early stages of the release, with middle and heavier compounds becoming more prevalent as the release ages and weathers. Figure 11 shows an example of groundwater partitioning of various CoCs from gasoline; note the significantly greater longevity of a compound like naphthalene relative to benzene.

These principles can be used with site specific analytic data to inspect for changes due to weathering, potential new releases or mobility, or other aspects. For a single release, there should be a gradual decrease in the molar fractions of the light end compounds like benzene relative to more persistent compounds. In a uniform setting, that will typically mean decreasing concentrations of light-end compounds like benzene and while heavier compounds remain fairly constant; e.g., one would expect the benzene/naphthalene concentration ratio to decrease over time. A sudden increase in the concentration or molar ratios can indicate new releases or migration, assuming other factors like changes in water levels are not the cause.

### 2.2.2 Chemical Transport Properties

There are a variety of chemical transport parameters. This discussion will be limited to the most relevant factors, with additional and extensive discussions in the references provided in Chapter 1 and in the bibliographic citations.

The 3-dimensions of the LNAPL plume (lateral and vertical extent) and its mass distribution within the LNAPL body are the source term for the chemical fluxes that occur in the dissolved-phase. The LNAPL plume geometry in the areal extent is the source control for mass fluxes in the vapor-phase and any associated risks.

The basic chemical properties of each CoC are also typically important to fate and transport estimates. Chemical factors and characteristics of importance include:

- Solubility
- Vapor pressure
- Molar or mass fraction of the CoC in the LNAPL
- Sorbance characteristics
- Octanol/water partitioning coefficient;
- Diffusion coefficients (aqueous and vapor)
- Biodegradability and half-lives.

For an active flow regime, dispersivity in the direction of flow, transverse, and vertical are important. It is also necessary to characterize the groundwater flow rates under which transport might occur. Vapor transport has analogous parameters under passive and active transport. These aspects of chemical fate and transport are typically estimated from field data and observations, aquifer testing, and through calibrating transport estimates to observations.

It is well known that most petroleum hydrocarbons readily attenuate in the subsurface (e.g., Rice et al., 1995; Mace et al., 1997; Weidemeir et al., 1995), with exceptions like oxygenated compounds under certain conditions. Demonstration of dissolved-phase plume stability and attenuation is typically demonstrated by two primary lines of evidence: 1) Temporal and spatial character of a particular CoC plume showing stable or contracting character; 2) Geochemical and biologic markers in groundwater or soil vapor. Of these, the first is the most important, with the second being an outcome specifically of the biologic processes that may be responsible for plume stability or contraction. Further, not all the processes involved in plume attenuation are biologic, so the first line of evidence encompasses those as well. For both lines of evidence, it is mandatory that the plume is adequately delineated. For instance, many of the MTBE plume length studies suffer from a lack of demonstration that those plumes are delineated in the vertical dimension, without which, the actual plume lengths are undefined. As noted above, strong downward hydraulic gradients are expected in island groundwater recharge areas; upward gradients are more likely in discharge areas, although any area may potentially be affected by groundwater production.

For an adequately delineated plume, one may simply map the CoC plume distributions over time, and interpret whether the footprint and center-of-mass is stable, contracting, or migrating. Depleted dissolved-oxygen in the source area and elevated carbon dioxide and methane are simple field-based biogenic markers indicating that degradation processes are ongoing.

### 2.2.3 Forensic Chemistry

Forensic chemistry is typically the investigation of the original source(s) of petroleum impacts at a given site or sites. That can include fuel type, refining character, original crude oil sources, degree of weathering, age, and other factors of relevance. The resources given in the introduction cover most of what any site investigator might need in this regard. The following paragraphs briefly cover some of the key forensic elements.

One of the simplest aspects of forensics is that fuel compositions have changed over time, primarily as a result of refining and/or regulatory changes. For instance, alkyl lead additives, oxygenates, sulfur, and refining changes all provide markers that can help identify the source and character of various LNAPL products released to the subsurface. Forensic chemistry evaluations are sometimes conducted as part of Tier II or 3 LCSMs, but are generally not needed for Tier I site models.

Site-specific information/context should also be considered in the interpretation of forensic chemistry. For example, the same chromatogram could be interpreted as mixtures of different fuels or represent degradation of a single fuel under methanogenic conditions. In this case, consideration of other site LCSM data could help determine which of the two conditions is most plausible (e.g., what types of fuel were in inventory at the release site; are there indications of methanogenic biodegradation such as low dissolved oxygen content in water, presence of methane, or other biomarkers).

### 3.0 LNAPL MODELING

Generally speaking, there are two types of LNAPL models, analytic and numerical. Both types require various input parameters that were discussed in the prior Chapter, as well as other hydrogeologic factors influencing the particular calculations. As with all modeling, the calculated results are only as good as the input quality and user judgment as to whether constraining assumptions are reasonable for the problem being solved. For any model, the HDOH will require backup regarding the key assumptions and limitations of the model, and a demonstration of a calibration to measured subsurface conditions against the model's predictions. A model that does not reflect reality, or at least reasonably bracket conditions, is invalid for that particular application. A model is only valid within its constraining assumptions. In general, the simpler the model, the more limiting its assumptions. The HEER office will always prefer evidence and interpretations based on site data over model results.

Analytic models simplify many of the conditions of state to result in a simplified and often heuristic estimate of LNAPL conditions; in multiphase mechanics, even "simple" models are quite complex and very sensitive to input selection. For instance, as discussed below, vertical equilibrium theory (VEQ) is a common analytic model for free-phase LNAPL distribution as correlated to the observed thickness in an observation well. Many analytic models are steady-state (time invariant), although some use a piecewise approach to simulate changes over time (e.g., API's LDRM model; Charbeneau, 2008). Because of the complexity and nonlinearity of the underlying multiphase mechanics, analytic models will fail most of the time at accurately representing subsurface conditions. However, because most of these models are based on sound science, they can assist in heuristic understanding of various aspects of LNAPL plume conditions. Where a model does not reflect ground conditions in a refined manner, it should at a minimum bracket those conditions and ranges reasonably well. One of the interpretive values of modeling is the thinking and tuning process necessary to constrain the model to have it give reasonable and representative results.

Numerical models solve the complex differential equations of transient flow and sometimes chemical transport for the multiple phases involved (recall Equation 1 above as an example). Most of these use mathematical approaches similar to those in petroleum reservoir exploration and unsaturated flow models in agricultural applications. Because of the calculation complexity, some numerical models limit the domain to fewer than 3 dimensions. Two-dimensional areal, radial, and cross-sectional models are common reductions in the problem geometry. Numerical models typically solve for complex problems that can include heterogeneity, transience, and other aspect that cannot be addressed with analytic models. Numerical models are not typically applicable to Tier I type of problems, but may assist in LCSM development for transport/cleanup at more complex Tier II and III sites.

#### 3.1 THE VERTICAL EQUILIBRIUM MODEL

VEQ theory relates the thickness of LNAPL in an observation well to the free-phase saturation distribution and volume in the formation (e.g., Parker & Lenhard, 1990; Farr et al., 1990). This VEQ theory is a key underpinning of many analytic and semi-analytic models

such as API 4715 (2002), the LNAPL Distribution and Recovery Model (LDRM, API #4760, 2008), ARMOS (1992) and others. Because VEQ is the basis for so many multiphase models, it is important to understand its basis and limitations. This is particularly true since LNAPL in wells is a common driver for site actions, typically with greater thicknesses thought to imply greater need for mitigation actions, which is not necessarily true. For an extensive VEQ discussion and development, see the references provided previously (e.g., Parker & Lenhard, 1990; Farr et al., 1990; API Interactive LNAPL Guide, 2004) and additional discussion in Appendix A.

The LNAPL thickness in a monitoring well can be used to determine the capillary pressures of the three multiphase couplets across that interval (water/air, oil/water, oil/air; see the equations in Appendix A). With these capillary pressures, the saturations of each phase (water, oil, air) can be calculated using the same procedures discussed above with the 2-phase air/water soil characteristic curves. That is, one selects a capillary model such as the van Genuchten or Brooks-Corey relationship, inputs the soil and fluid capillary parameters describing the system, and then calculates the associated phase saturations as a function of the capillary pressure spectrum.

VEQ theory does not account for residual LNAPL that is not in hydraulic communication with the monitoring well; the estimates account only for the mobile-phase product. When LNAPL disappears from a well (perhaps due to water table fluctuations), it does not mean it has vanished from the formation. Rather the disappearance in the wells means it has become trapped within the pore space as residual LNAPL that may reappear when the water table falls (e.g., recall Figure 7). So if one calculates the mobile-phase volume at a low water table stand, that estimate will result in a mobile-phase volume much greater than at a high water table. Further, and this cannot be overemphasized, because the mobile-phase volume is typically a small fraction of the total, these VEQ estimates *are not* mass estimates of the total plume, but only of a small but possibly an important fraction of that total. The longevity of risk presented by the plume is a function primarily of the total mass in-place. As will be discussed further in the subsequent LCSM examples, evaluation of measured saturations/TPH, gauging hydrographs and other data will help place VEQ estimates within a broader site context.

As discussed above, the capillary functions are nonlinear and therefore so are the VEQ estimates in terms of saturation, volume and mobility. This will be the first example of the sensitivity of these controlling factors, and in fact, demonstrating this sensitivity is one of the values of the VEQ family of models. Figure 6 shows a family of gasoline saturation curves for an equilibrated well thickness of 1m (~3.28-ft) for the same soil capillary characteristic curves shown previously in Figure 5; Figure 12 shows the contrast between gasoline and diesel fuels for two of those soil types (fine- and medium-grained sand).

There are many observations to these example calculations, as summarized in Table 2 below; calculations such as these can be easily performed using the API Interactive LNAPL Guide (2004). As observed, the gasoline saturation ranges across three orders of magnitude depending on soil type, with fine-grained soils containing the least LNAPL and the contrast in area mass is similar. Again, recall that the capillary pressure distributions are identical, only the soil capillary properties differ. More interesting from a risk and recovery point of view is that the effective mobility spans more than 8 orders of magnitude. So for the same oil thickness in an observation well, there is

fundamental difference in whether that LNAPL poses a likely risk or whether it is recoverable. For the finer-grained materials (and assuming no secondary permeability features), the answer is clearly no, the LNAPL is neither mobile nor recoverable to any significant degree. For coarser grained materials, the opposite may be true. One can also observe that diesel has much lower saturations, mass and mobility than gasoline for otherwise the same conditions. So as noted previously, a given well thickness alone has no technical context without these supporting estimates and observations (or other similar multiphase calculations).

TABLE 2: VEQ ESTIMATES FOR VARIOUS SOILS AND LNAPLs

Soil Type	LNAPL	Max Oil Saturation	Area Mass kg/m <sup>2</sup>	Max Conductivity (m/d)
Clayey Sand	Gasoline	7.13E-04	0.08	1.13E-08
Silty Sand	Gasoline	3.59E-02	3.46	3.76E-04
Fine Sand	Gasoline	2.13E-01	20.73	4.54E-02
Medium Sand	Gasoline	3.14E-01	27.55	7.20E-01
Coarse Sand	Gasoline	6.39E-01	56.17	4.74E+00
Fine Sand	Diesel	1.40E-01	12.86	6.08E-03
Medium Sand	Diesel	2.25E-01	18.71	1.15E-01

One other observation is critical to these estimates and their applicability. If fine-grained materials were truly represented by these calculations, then plumes within those materials would not migrate to any significance in the subsurface and they would all be small volume. The fact that we often observe widespread plumes in fine-grained materials indicates that the controlling parameters are not represented by the associated soil characteristic capillary curve. Rather, fine-grained materials often exhibit secondary permeability features and these allow the otherwise unexpected migration of LNAPL in the subsurface. This is a case where the VEQ models suggest one outcome, but observations another. Always trust observations first and foremost and recognize that there is nothing wrong with the model except the assumption of no secondary permeability features.

Because the assumption of VEQ is independent of soil type or heterogeneity, it is also possible to execute the same estimates for a layered lithology across the LNAPL interval. Figure 13 shows such an estimate for a three-layered heterogeneous condition, with each layer considered explicitly. Recall that the capillary pressure distribution is still uniform at equilibrium, the variance within each layer being determined by the contrasting soil capillary properties. In site specific cases where the mobile-phase LNAPL exists vertically across different lithologic horizons, one would use a multilayered capillary calculation to evaluate mobility, risk and remediation scenarios (see example below). It typically is inappropriate to average lithologies in a multilayer setting because the coarsest grained zone will have a much greater mobility and saturation than finer-grained zones, and averaging is therefore non-conservative (underestimates mobility and risk).

Finally, the key question for this model (or any other) is whether this VEQ estimation technique works. Here we are defining “work” to mean whether the VEQ model accurately reflects measured subsurface saturation distributions? The short and painful answer is “sometimes.” In general, this VEQ modeling approach is probably best thought of as a heuristic model that informs but is often not fully reflective of ground conditions. It has the best probability of accuracy when conditions are relatively permeable, water tables steady, and the release is old enough to exist under equilibrium conditions. Figure 14a shows a local Hawai’i example of predicted versus measured LNAPL saturations for a heterogeneous and tidally influenced coastal site. As observed, the VEQ model does a poor job of matching site specific observations even using site specifically measured parametric values; one could tune the input parameters to better enclose the data, but the model would still be a poor match to site data. Figure 14b shows a case where VEQ predictions match well with measured saturations at a site with a uniform homogeneous sand lithology and stable water table conditions for the period modeled. So again, the more heterogeneous and transient conditions may be, the less likely that VEQ estimates will be reflective, though they may be informative if executed heuristically. In our experience, variable conditions are more generally reflective of most sites in Hawai’i and therefore VEQ is expected to diverge from ground conditions in the majority of cases. The data plots in the prior figures are simple to construct and provide the litmus test for the VEQ model versus data observations.

Remember as well that VEQ is not a dynamic model that makes estimates of plume-wide conditions over time, but rather only local area conditions around a particular monitoring well assumed to be at equilibrium. Here is a quick example of how misapplication can lead to highly erroneous results and decision making. As discussed in Chapter 2, LNAPL plumes grow in a highly transient manner. The first LNAPL arrival at a nearby monitoring well will be a small thickness that will increase over time. If one were to analyze that initial small thickness, the estimate would suggest very small mass and mobility with respect to oil. However, that would be completely erroneous because the plume is undergoing migration (non-VEQ conditions, etc.) that presents a significant potential risk due to that transient mobility. Clearly VEQ estimates are ***not*** appropriate if an LNAPL plume is laterally migrating and spreading. Equally clearly, one ***must know*** some things about plume conditions before using any particular modeling method, and that knowledge comes from developing the LCSM. If there is a gap in sufficient knowledge, then that should be filled. Non-recognition of the signs of plume mobility can allow impacts to occur that could otherwise have been managed and prevented had that mobility been understood. Signs of mobility may include new arrivals of LNAPL at previously non-impacted sentry wells, new dissolved-phase arrivals, recency and magnitude of releases, and other field-based observations. In short, application of the VEQ model to mobile plumes is fundamentally inappropriate and will typically result in misleading results (i.e., model constraints do not match actual conditions).

### 3.2 GENERAL LNAPL MODELS

More general LNAPL models include those that can address heterogeneity, transience, multiple releases, cleanup mechanics, and contaminant fate and transport among other phenomena. Most often, these are numerical models, although some semi-analytic models can address more complex aspects of multiphase and contaminant transport processes.

The purpose here is to elucidate when and why to use more complex models and how to ground-truth the results (e.g., compare the results with measured site data). The discussion will not identify any particular models, as that decision is site and problem specific. For instance, if one were interested in multiphase cleanup mechanics only, then it would be necessary to select a model that accounts for 2- or 3-phases of active flow (depending on the cleanup method; any air-based technology would typically require consideration of 3-phase flow). It may or may not be important that the model consider contaminant transport or recovery. If one were interested in the likely contaminant distribution around a stable LNAPL plume over time and the determination of the longevity of that plume, then it might be unnecessary to have a dynamically active LNAPL phase and rather a static chemical source mass could be simulated. The site specifics and questions to be addressed determine the model selection and approaches, not the other way around. Misapplication of models often results from attempting to force a problem into model assumptions that are not technically justified. Using simple models for a complex problem is one example of this.

The determination of whether a model is needed or not to estimate particular conditions over time or distance is typically made when site specific data, or additional data cannot address pertinent aspects of the LCSM. For instance, an LNAPL plume with a limited history of gauging and analytic data sampling may require modeling to determine its long-term chemical fluxes and risk. Another example could be an expected future change to groundwater flow and transport conditions, perhaps by water production changes or rising water levels (e.g. sea level rise, high precipitation events and groundwater inundation). Could those changes influence the mobility of LNAPL, its contaminants or risk? Yet another example might be that of a suspected new release on top of an existing release with the potential to transiently change the migration and risk conditions. Transient and heterogeneous considerations are two common problems that lead one to modeling solutions.

It is well accepted that even with simpler groundwater flow models (simple being relative to a single phase rather than three), there are rarely well validated models. A validated model is one that has been calibrated to past and present conditions and afterwards is shown to have accurately predicted future conditions prior to those occurring. So, by extension and given the added complexities of multiphase flow, even a complex numerical multiphase model will not likely be fully representative. But, the exercise of constructing the model and tuning it to known data and conditions will almost always yield insights that would not have been evident otherwise. Sometimes those might be critical data gaps in site understanding, other times certain processes may rise up as being of key importance.

For almost all multiphase models, a key calibration data set is the model estimates of mass and saturation distribution as compared to ground measurements. As noted above, those might be soil cores tested for saturations by a petrophysical laboratory, TPH conversions to saturation, or geophysical logs like laser-induced fluorescence. If the model initialization under or over estimates in situ saturations and mass, the results will be suspect even if the methodology is otherwise robust. As noted above, the HDOH will only accept models with associated calibration evaluations and justification for the model applicability to the problem(s) being addressed.

Perhaps one of the best uses of more complex modeling is in remediation design. Targeting of the three-dimensional source of LNAPL in the subsurface can be addressed by rigorous models. Recall that a description of the 3-D distribution of the LNAPL body is a fundamental element of the LCSM, regardless of the Tier level. In executing these types of models, it becomes clear that many industry rules of thumb for remediation design, such as the radius of influence, have little applicability to predicting the success or failure of a particular remedy to meet its specified endpoints. This is because these rules of thumb have little or no relationship to the multiphase processes that allow remediation targeting to be successful. For instance, a site with submerged LNAPL would have the same pumping ROI as a similar site with little submerged LNAPL, but the remediation approaches would necessarily be much different because of that submergence. In short, most remediation rules of thumb tend to be simplistic versus the underlying multiphase mechanics that are inherently complex.

#### 4.0 THE LCSM AND USES OF SITE DATA

As noted in the Introduction, the LCSM is a written and pictorial presentation of the state of knowledge regarding site specific LNAPL plume conditions (recall Figure 2). In turn, the LCSM informs site mitigation decisions based in part on the potential risks to people, the environment and groundwater resources. Although the term “conceptual” is part of the LCSM definition, many of the parameters and evaluations associated with the LCSM are rigorously quantitative.

The development of an LCSM usually follows a tiered process, beginning with a simple model and moving to a more complex model as site requirements and uncertainties suggest. Building a more advanced LCSM, often with additional data collection and analysis, is typically needed when fundamental questions about risk and/or cleanup cannot be answered with existing site data or appropriate literature values. As shown earlier in Figure 1, there are a number of site specific considerations that affect the level of complexity of the LCSM. The general expectation for each LCSM Tier was discussed in Chapter 1.

The sections below address potential uses of site specific information to help build an LCSM and to help link the LNAPL source zone to other typical investigation data. This approach extends existing standard site data into a multiphase context, allowing for a more robust understanding of LNAPL plume conditions. Appendix B provides an LCSM checklists to consider when constructing the model, figures and supporting discussions.

After covering some of the key site specific data uses, this Companion Document will discuss more advanced data collection options, though not exhaustively. The types of advanced data augmentation required depend on the site-specific elements of the LCSM that cannot be adequately addressed with existing information. For instance, if data is too sparse to characterize the dimensionality of the LNAPL body, then perhaps additional coring, laser-induced fluorescence, or other characterization methods might be considered. If the chemical character of the LNAPL is important to evaluations of risk or sources of the release, then perhaps forensic chemical analyses may be in order. In short, the site-specific data gaps drive the data collection needs and methods.

Before exploring potential uses of site data and the augmentation thereof, it is useful to simply consider what elements are typically embedded in an LCSM, as outlined below. As can be observed, the first five are related to typical site assessment evaluations, the remainder are dependent on those.

1. Site layout, current and past land use, responsible parties and other general geographic characteristics.
2. Hydrogeologic conditions need to be described with adequate clarity (i.e., sufficient to make informed and representative risk and cleanup determinations). This includes, but is not limited to the following elements:

- a. Geologic setting and types of earth materials likely to be present and their characteristics;
  - b. Hydrostratigraphic conditions include important lithologic and hydraulic factors that control the movement of water, LNAPL and vapor in the subsurface;
  - c. Groundwater/saturated zone conditions, synoptic fluid levels, potential rates of flow, background water quality, and connectivity to surface water or other discharge points;
  - d. Links between the above and the LNAPL distribution and gauging data previously discussed.
3. Plume delineation includes the three-dimensional distribution of the LNAPL and daughter plumes. Delineation is a common goal of site plume investigations, and often more can be gleaned by broadening the uses of site data (as discussed below). The plume distribution in turn informs potential flux and risk to relevant receptors.
4. Release conditions of the LNAPL plume are important for understanding the plume context, as discussed previously. Because LNAPL transport is highly transient, the known, suspected or inferred release conditions are important for several related reasons:
- a. The timing of release bears directly and strongly on the probability of remaining mobility.
  - b. Significant differences in plume distribution, risk and cleanup amenability are expected depending on the nature of the release. A slow, continuous leak will be distributed much differently than a short-term release of a similar volume. In other words, the rate of release can be important in building the LCSM.
  - c. The release conditions also encompass the source or sources of the release(s). It is often the case, even at small sites like service stations, that releases have occurred at more than one location, time, and rate. The potential risk from one release area may be different from another. For instance, a line or dispenser release will almost always have a near-surface source (a potentially strong source of vapor impacts). A leaky UST may have a deeper expression of impacts that have a different risk character.
  - d. The site properties involved and potentially responsible parties are also of course relevant to this aspect of the LCSM.
  - e. Tier I LCSMs typically have relatively simple release conditions or a low sensitivity to those conditions with respect to risk, cleanup and site closure.
5. Characteristics of the LNAPL or LNAPLs present in the subject release(s). This includes both the physical and chemical character of the LNAPL.
- a. Physical characteristics, discussed previously, include density, viscosity, interfacial tensions, and descriptive factors including color, clarity, and others.
  - b. Chemical characteristics refer to the component makeup of the particular LNAPL(s) present, particularly with respect to the CoCs and their mass or molar fractions within the LNAPL(s).

- c. For a Tier I evaluation, these aspects can be estimated from site analytical data and literature values for common fuel types.
6. Assessment of the mobility or stability of the LNAPL plume under prevailing and potential future conditions. From the combination of the above information, data, and evaluations, a plume migration/stability assessment is a critical element of the LCSM. Where an LNAPL plume is mobile and migrating, it creates expanding potential risk zones in all phases (LNAPL, water and vapor). Where stable, a plume will present a known and decreasing potential future risk.
    - a. This evaluation, regardless of the LCSM Tier level, always starts with site specific data and observations.
    - b. Supplemental petrophysical data and other more advanced delineation methods may be applied when standard site data do not alone allow a definitive assessment of plume migration/stability.
  7. Receptors need to be identified whether human, groundwater (resource) and/or sensitive habitats. Complete or potentially complete pathways to those receptors should also be identified. While very important to the LCSM, regardless of the Tier level, identification of receptors is usually straightforward.
  8. Risk screening is based on all the above elements to assess whether the LNAPL plume conditions create a present or future risk to receptors. Part of the assessment will deal with the magnitude and likelihood of actual risks.
    - a. It is important to evaluate imminent threats at the time of release discovery. If the release is recent, receptors are nearby, or any other factors that suggest an imminent threat, then immediate interim corrective measures should be implemented.
    - b. The Hawai'i DOH will accept hazard screening methods as outlined in the HEER Office TGM and HEER Office Environmental Hazard Evaluation Guidance.

#### 4.1 USES OF STANDARD SITE DATA IN THE LCSM

As noted, most of the commonly collected site data can be used directly or interpretively to develop elements of the LCSM. Two of the most important LNAPL related features to understand are distribution and mobility/migration. The LNAPL distribution in three dimensions is important because it is directly related to potential risks and site remediation design. LNAPL mobility/migration is critical because of its relation to potential receptors and/or exacerbating impacts to the groundwater resource.

The summary of potential uses of site specific data listed below follows the LCSM elements as listed above. There is recognized redundancy in certain aspects. For instance, determination of the source or sources of an LNAPL release has distinct parallels to its delineation and geometry in the subsurface. This redundancy is useful, however, as the interpretive intent of the data use is for distinctly different elements of the LCSM.

Lastly, the HDOH will require that all important site information, data, and evaluations be inclusive to the LCSM. It is difficult to review an LCSM absent that information being at hand, as opposed

to by reference. For instance, an historic aquifer test may provide good quality information about the hydraulic characteristics of the saturated zone at a release site. Appending the relevant analyses and conclusions of that report to the LCSM allows that information to be quickly and efficiently reviewed and understood.

#### 4.1.1 General Site Characteristics

This section of an LCSM (or CSM) is common and foundational. It sets the general context for the release site by providing its layout, operational history, geographic setting, and other elements of relevance. The level of detail follows the Tier level of the LCSM. The more complex and long-lived a release site and its operations, typically the more complex the site background section. Among other items of interest, the HDOH will need an understanding of potentially responsible parties for releases.

#### 4.1.2 Hydrogeologic Conditions

Hydrogeologic conditions provide a telescoping context to site plume conditions and potential risks. The area or regional setting helps to set some context for site specific conditions. For instance, is the site in a groundwater recharge or discharge zone? If in a recharge zone chances are good that there are downward vertical gradients and dissolved-phase plumes may dive as a result. In discharge zones, the opposite is typically true. Documenting and understanding groundwater use in an area is also important, both as a potential receptor and as an influence to area groundwater flow and behavior.

Area and regional conditions also put context on background water quality conditions. Groundwater geochemistry is developed based on the lithologic materials through which natural waters flow. Water inconsistent with the background geochemical system may suggest an alternate source, such as leaky water or sewer pipes or other man-made artifacts.

The lithologic and formation characteristics of the geologic units helps set some expectations for plume behavior. For instance, in known fractured rock units, flow rates of contaminants can be very high and also difficult to characterize. The nature of the deposition of the formations of interest can also provide good information on the likely degree of heterogeneity and the scale of that.

The history of water levels in an area is another useful part of the hydrogeologic context. As mentioned previously, an LNAPL plume will commonly find its way to the deepest water level interval over the course of the plume's life span. It is common to find LNAPL many tens of feet below present-day water levels, reflecting historic lows due to drought, groundwater production, or other factors. Again, do not let the fact that LNAPL is a "floaters" obscure the possibility that it may be present at depths far below the present day water table.

The USGS maintains a robust suite of ground- and surface water monitoring stations where one can often derive an historic view of water conditions near a particular LNAPL release site.

<https://maps.waterdata.usgs.gov/mapper/index.html>

Moving on to site specific hydrogeologic aspects, one should use the site data to determine several aspects that will affect the risk, cleanup and plume longevity outcomes. These include:

1. Direction and magnitude of groundwater flow.
2. Assessment of vertical groundwater gradients, and if present, whether they indicate the need for deeper plume assessments.
3. Hydrostratigraphic conditions within and around the LNAPL plume, the degree of heterogeneity, secondary permeability features and other aspects that could affect plume conditions.
4. Surface water discharge locations, if any, where contaminants may encounter those surface waters and environments.

#### 4.1.3 Hawai'i Specific Hydrogeologic Considerations

Probably the two most significant Hawai'i specific hydrogeologic considerations are the formation of the islands from shield volcanic activity and the large amount of rainfall in certain areas. A third aspect is potential tidal influences on coastal release sites. Finally, an engineered aspect of hydrogeology is the Underground Injection Control (UIC) program present on all the islands; this boundary delineates drinking water on the inland side and non-drinking water seaward, as discussed below. We will address each aspect below along with some of the implications of this setting.

In overview, the hydrogeology of the Hawaiian Islands can be subdivided into two basic, geologic systems - "basal" groundwater in fractured and porous basalt and groundwater in locally onlapping, "caprock" marine and alluvial sediments (Stearns 1966, McDonald et al. 1983). Caprock formations are characterized by inter-bedded, unconsolidated, marine to alluvial clays, silts, sands, gravels and coralline sedimentary "caprock" deposits with locally occurring layers of late-stage, volcanic tuff and basalt. The deposits reflect past, higher sea stands and can extend inland to elevations up to 200 feet above current, mean sea level. Inter-bedded tuffs and basalt units reflective of late-stage volcanism can also be found in some areas. The caprock formations overlie the basal, basalt aquifers that form the primary groundwater aquifers on the islands.

In general, all groundwater inland of the UIC lines should initially be treated as a current or potential source of drinking water, provided it is present in a suitably productive geologic formation. (HDOH 1995; see also HEER EHE guidance, HDOH 2011 and updates and Section 6 of the TGM). Reference can be made to the Water Resources Research Center (WRRC) Aquifer Identification and Classification reports to evaluate the utility of the groundwater on a more site-specific basis for each island (e.g., Mink and Lau 1990-1993). Groundwater situated seaward of the UIC line is generally considered to not be a potential source of drinking water due to high salinity, low permeability and production, and/or historic contamination.

This information is then used to select soil and groundwater Environmental Action Levels (EALs) in the HEER Office EHE guidance (see Section 13). In general, soil and groundwater action levels

are more stringent for sites that threaten a potential source of drinking water and are located within 150 meters of a surface body of water (Tier 1 EALs). All groundwater action levels consider potential discharges to aquatic habitats as well as other potential environmental hazards, regardless of utility as a potential drinking water resource.

Although the term is loosely used, not all groundwater is situated in a geologic formation that could be classified as an "aquifer." By definition, an aquifer is a rock or soil formation of moderate to high permeability that is capable of producing a sustainable quantity of water. By contrast, an aquitard is a layer of low permeability and an aquiclude is an impermeable layer. It is important to note the difference of permeability and porosity here. A geological formation or layer can be of high porosity, but low permeability (e.g., clay). Permeability implies that pores (or fractures) are connected and water can be transmitted through the rock layer. The term also implies that the groundwater has potential usage for drinking water, irrigation or industrial purposes. Hydrogeologic criteria for potential exclusion of a given occurrence of groundwater from consideration as a potential source of drinking water typically include

1. Total dissolved solids in groundwater is greater than or equal to 3,000 mg/L; OR
2. Water bearing unit is not sufficiently permeable to produce an average, sustained yield of 200 gallons of water per day.

Groundwater in coastal areas and geothermal fields, for example, may contain levels of dissolved solids that make the water unsuitable as a source of drinking water. In addition, the permeability of soils and sediments that lack a significant amount of coarse-grained material (or fractures, in the case of bedrock) may be too low to allow for an adequate, sustained yield of groundwater. Unconsolidated geologic units that consist of less than 20% sand-size (or larger) material or more than 30% clay-size material are typically not considered to be viable "aquifers" or potential sources of useable groundwater (inferred from Fetter 1994).

Much of the basal groundwater is indeed situated in viable aquifers. This groundwater becomes confined and artesian as it migrates seaward and becomes trapped under the overlying caprock formations. Springs of fresh groundwater from basal aquifers are common along the shoreline areas of the islands. Groundwater in the caprock units is generally unconfined, although local confining conditions may exist due to the presence of tight, clayey units. Permeable carbonate units in some areas of thick, caprock sediment serve as aquifers for irrigation purposes (e.g., the Ewa plain area on O'ahu), although the salinity may be too high to serve as a drinking water resource without treatment. Most of the groundwater encountered in caprock areas is otherwise not situated in a formation that could be considered a viable aquifer, although it may be "ecologically important" due to its connection and discharge to nearby, aquatic habitats (see WRRC reports; see also Section 13 and HDOH 2017 EHE guidance).

These distinctions are important to recognize, since requirements for remediation of discovered contamination and eventual well abandonment depend in part on the nature of the groundwater encountered. The clayey and silty nature of the caprock sediments can impede adequate development of monitoring wells and require filtering of samples. False detections of "dissolved-

phase" metals that slightly exceed HEER Office EALs are common even after filtering in some areas (e.g., low ppb concentrations of lead, barium, selenium, nickel, etc.).

#### *4.1.3.1 Volcanic Hydrogeologic Setting*

Volcanic activity in Hawai'i has produced the bulk of the land mass of all the Islands, with the youngest being the Island of Hawai'i at the southeast end of the chain and the oldest being Ni'ihau and Kauai to the northwest (USGS, 2017). The nature of this type of formation is important to understanding the hydrogeology of the Islands (e.g., Figure 15). Shield volcanic activity forms the majority of the land mass, with post-shield activity producing additional surface materials with some rejuvenation stage activity from reactivation of volcanic activity. The rejuvenation volcanic stage generally consists of typically lower permeability materials like ash and cinder cones, with some exceptions.

Two salient features of this volcanic land-building setting are the high permeability of the shield lava aquifers, along with discrete locations where post-shield lava deposition is also of high permeability with fractures. This high permeability coupled with areas of high recharge due to high precipitation can mean rapid transport of the groundwater plume.

Besides flow along fractures, flow along contacts or other natural preferential pathways can be important. The two dominant forms of lava flows in Hawaii are Pahoehoe and A'a lava flows. Pahoehoe flows are usually lower viscosity lava flows that also develop lava tubes. These lava tubes may be preferential pathways. Due to the low viscosity, Pahoehoe flows develop a large quantity of rounded vesicles, which provide a large storage capacity for LNAPL if released into this system. A'a flows are typically formed by more viscose (cooler) lava. This leads to massive flows with rare stretched vesicles in the center of the flow. However, clinker zones often form at the tops, bottoms, and sides of these flows through the breaking off of parts of already solidified lava on the outside of the flow. These clinker zones are networks of blocky lavas with lots of gaps in between where LNAPL easily can be stored or transported.

The presence of fractures in many of these lavas can create a complex flow regime. For LNAPL, the concepts discussed earlier hold, but if fracture apertures are relatively large, there is little in the way of capillary forces to resist LNAPL flow. For both water and LNAPL, flow in fractures can be both rapid and widespread.

Characterization of fracture networks and associated flow is notoriously difficult. One of the key features we wish to describe is the nature of dominant, active, and connected flow within the fractured system. From that, we want to develop this aspect of our LCSM to address CoC distribution, transport, and potential receptor impacts now and in the future. A few of the potential techniques to do so are discussed here, with a large number of additional characterization methods described in the resources provided in Section 1.4 and the bibliographic references therein.

One very useful fracture characterization approach is to evaluate outcrops of the same formation and setting in road-cuts, cliffs or other erosional features. Things to observe and document might include the following:

1. Fracture orientation, density and distribution
2. Bedding plane voids between lava layers
3. Fracture in-filling
4. Void fillings by hydrothermal alterations (e.g., in caldera zones)
5. Presence of lava tubes or clinker zones
6. Fracture aperture, how large the fractures might be
7. Evidence of water movement and its preferential flow patterns
8. The nature and fabric of the rock materials to compare to site sampling logs
9. Geographic location and elevation and correspondence to site setting
10. Other features of note like dikes, weathering, erosion, etc.

Other tools for fractured rock characterization include single location downhole testing methods versus methods that characterize broader sections of the fractured rock aquifer. A few of each are discussed below. The majority are down-bore methods that require an open borehole to run. Resistivity and gamma logging tools are available that can penetrate a PVC casing, but those logs are not the most refined in fracture identification. Packer, tracer, and flow testing can also be completed in a finished well, assuming it is screened in the necessary fracture zones.

Geophysical testing methods have long been used to assist in fractured rock characterization. An acoustic caliper or standard caliper measures the standing borehole diameter, with fractures often indicated by widening of the borehole across a specific interval. The acoustic caliper measures in a full circular sweep, and some standard calipers do the same (some do not, but have 3 or more arms). Caliper logs are often coupled with standard geophysical testing such as resistivity, gamma, temperature, self-potential. Figure 16 shows an example of a standard caliper log, combined with other downhole logs, with the associated fracture zone identification. Together, these downhole tests can assist in identifying fracture zones intersecting borings and wells. For any of these methods to be applied, the boring must be able to stand open long enough for the logs to be run.

An acoustic televiewer works on similar principles except that its output is a visual log (Figure 17). The televiewer tool images a 360-degree rotational image of the borehole wall from which fractures, their orientation, dip, and apparent apertures can be derived. Digital borehole scanners produce a red-green-blue spectrum response to the white light signal from the borehole wall and can provide high resolution information on the fracture condition. Standard downhole video logging can also be useful to observe potential flow zones and any alteration. Keep in mind that rotational logging is often presented on a continuum chart over 360-degrees, which makes fractures appear to undulate based on their dip (Figure 18). The down-dip expression in the boring is of course lower than the up-dip side with continuity between the two. In fact that is how the dip of the fractures can be determined by the trigonometry.

Because fractured settings often have differential flow of groundwater within the matrix, downhole flow monitoring is a good test to use in conjunction with temperature and conductivity to characterize fracture flow zones (zones with similar character). Colloidal bore scopes are another tool to measure the rate and direction of flow by monitoring the dispersion of a colloidal solution within a wellbore at different depths. Definition of the vertical component of flow is one benefit of this method, but a standard impeller, thermal pulse or digital sensor will produce faster results and allow more profiling to be done in a given amount of time and effort. The focus with these logs is on discrete flow rates, whether as inflow or outflow, vertical movement within the borehole, changes in water character (based on electrical conductivity and temperature), or other factors that suggest dominant fractures with active flow.

Test methods that characterize more broadly than just the boring are also useful, particularly in concert with some of the methods above and others. Tracer testing is one such method that has the potential to demonstrate hydraulic connectivity between fractures and boreholes. Tracer tests introduce a nontoxic water soluble compound into discrete fractures within a boring/well, and monitor other locations for the arrival of that tracer. Commonly the boreholes are packed off within specific intervals that are thought to interconnect based on prior data collection and interpretation from one of more of the borehole test methods noted above. Tracer testing can provide direct evidence of interconnectivity and flow rates within fracture sets. However, depending on the distance of travel and whether or not fractures are truly connected, testing requires sufficient time to either demonstrate that connectivity or through absence of response, to suggest limited connectivity or limited flow.

Well controlled aquifer pump testing is another method of characterizing fracture networks. Pumping with a suite or set of fractures will cause hydraulic responses in adjacent boreholes connected to the same fracture sets. As with tracer testing, zones of interest are often isolated with packers to test different intervals suspected of being important to the flow regime. Interpretation of these pump tests can be complex (and outside the scope of this Companion Document), but fundamentally, rapid responses at adjacent locations indicate direct connectivity of the given fracture sets, whereas delayed or minimal response suggests limited connectivity.

There are many other geophysical, hydraulic, and other test methods for characterizing fractured rock settings. Our discussion has been limited to those that are most available and applicable to the setting of the Islands of Hawai'i. Again, the key determinations are whether the fractured system is contiguous with the LNAPL or dissolved-phase impacts, and if so, how contaminant transport and the spread of impacts might behave. One key sensitivity is the size of the apertures combined with their interconnectivity; generally large interconnected apertures create the greatest rate and distribution of contaminant spreading. The key conclusion of the analysis is whether or not sensitive receptors are likely to be impacted now or in the future by the LNAPL or dissolved-phase plumes.

#### *4.1.3.2 Coral Deposits*

While not as prevalent in distribution as volcanic materials, coral deposits are also commonly observed on the Islands, particularly the older islands and in near-shore settings. In many ways, coral deposits parallel those of the fractured rock systems, but at a smaller scale and with more discontinuity. The same types of mapping and tests noted above can be useful for coral deposits.

One aspect of LNAPL behavior in corals and limestones is there can be a tendency for these materials to be oil-wet. That means LNAPL moving within these materials has a higher propensity to become permanently trapped as it passes through the matrix. This also makes cleanup more difficult as the residual mass will often be stored in the smallest pore spaces of the overall matrix. Because of their prevalence below the water tables and outside most drinking water zones, corals (while complex) are typically less important than the volcanic fractured rock system, in most cases.

#### *4.1.3.3 Island Hydrology*

As noted, the Islands also differ from many setting in the widely varied precipitation rates between islands and geographic setting upon each island. Figure 19 from the University of Hawaii shows this dramatic difference, with typically high elevations and eastern portions seeing much greater precipitation than lowlands and to the west.

Between the large topographic contrasts and the contrast in precipitation, there is a large amount of water movement (ground and surface) between areas receiving high quantities of rain and the lowlands. This creates large vertical hydraulic gradients in some areas, with downward flow in recharge areas and upward flow in discharge zones, overprinted to varying degrees by pumping and seawater injection controls.

#### 4.1.4 LNAPL Release Characteristics

The character of an LNAPL release can be simple or complex. Typically, simple plumes are from a single, identifiable source of a one-time release. This could, for example, be associated with a one-time release from a gasoline service station. Conversely, complex plumes are those where multiple product types over a long-time frame may have been released to the same general subsurface area; these types of plumes are common at refineries, long-operating terminals and multiple product pipelines (among others). Additional complexities are associated with plume aging and weathering, or ongoing releases.

Soil samples within or near the LNAPL smear-zone are good indicators of product type; sampling should not stop at the water table, but rather continue through the impacted interval until non-detects are reached. Soil analytical laboratories will usually characterize TPH ranges against common fuel standards like gasoline, diesel, kerosene, jet, fuel oils, and others. From these results, one can assess

the likely generalized composition of the LNAPL within the smear-zone. Direct sampling of the LNAPL phase, when present, results in similar laboratory analytic data. Acquiring the gas chromatograms typically associated with these lab test results can be useful in identifying potential differences between samples.

Once the LNAPL product type (or types) is known, one can infer the physical properties from a wide range of literature values on the subject. The EC Oil Properties database is one good resource, although physical properties are not always listed. The API ILG (2004) also provides tables of physical properties of common petroleum products, as does API #4715 (2000). As discussed previously, the viscosity and interfacial tensions are the most sensitive in mobility assessments, with density varying over a smaller range. Clearly, if it is important to site specific mobility/risk evaluations and to reduce uncertainty, one can also have these properties measured directly by a petrophysical laboratory.

LNAPL chemistry can likewise be inferred from literature values, such as those referenced above and in the forensic chemistry citations. However, in general, a better approach is to use site specific groundwater data to infer the LNAPL chemistry of key CoCs. For monitoring wells within the LNAPL smear-zone, groundwater data will often reflect the molar composition within the LNAPL feeding that plume. One can use Raoult's Law (discussed in the references and Appendix A) to convert a site-specific groundwater concentration to its equivalent molar fraction in the LNAPL.

As an example, let us assume a site has a gasoline plume with a source-area dissolved-phase benzene concentration of 16.5 mg/l. We know from a variety of references that pure-phase benzene has a solubility of approximately 1,780 mg/l. This example results in a benzene molar fraction in the LNAPL of  $9.3 \times 10^{-3}$  (i.e.,  $16.5/1,780$ ). In general, these estimates are done only for wells with the highest concentrations, and also considering whether or not there are likely dilution effects by together considering the concentration ranges, fuel type, distribution, and hydrogeologic setting. In general, when the resulting molar fractions are within the range expected for a given fuel type (accounting for weathering), then the approximation is likely relevant. Where dilution may be evident, it is also possible to perform low-flow vertical profile sampling of groundwater at a well or wells in the LNAPL source zone. This data will often show the zones of highest concentration, in turn suggesting proximity to LNAPL.

In summary, without performing any advanced testing, we can arrive at reasonable estimates of the LNAPL physical and chemical character. If the uncertainty within those estimates and interpretations cause uncertainty in the conclusions of the LCSM that would suggest site-specific measurements may add value to decision making. Conversely, if within the expected product type ranges there is little variation in the outcome of the LCSM, then further site-specific testing would not be indicated for this facet.

As mentioned, the LNAPL release conditions affect the geometry, mobility, and other aspects of the LNAPL plume. While informative, this element of the LCSM is not as important as some of the

others (like mobility). Sometimes the release conditions are well known and documented. These known release sources and conditions are often detected through sensors or alarms designed to detect failures in the storage, transport, and dispensing systems. Often though, the release is detected after the fact through other means. When this is the case, one must combine available lines of evidence to ascertain the likely release conditions.

The type of products present and their likely age is one indicator of potential release sources and the conditions of the release. The geometry of the LNAPL plume, as discussed above, is another indicator. Larger single releases commonly show a thicker zone of impacts around that source. Similarly, we know that virtually all release start near-surface. So for instance, if site data show the initial impacts at 30 feet below grade (fbg), we know that the actual source is likely much shallower. Perhaps a few fbg for pipelines and transfer piping, to 10 - 15 fbg for most USTs. Connecting the "dots" is a useful way to distill some indications of the LNAPL source and release conditions.

#### 4.1.6 LNAPL Plume Delineation

The LNAPL 3-D delineation includes potentially three components: 1) the mobile-phase distribution;  
2) the residual-phase distribution; and 3) any occluded residual phase that could become remobilized. All three will typically be present in cases where floating observable LNAPL is or has been present in observation wells.

Soil borings are a common method of plume investigation. While they may vary in detail, most include at least some elements that can assist in LNAPL delineation, at least in a bulk sense. The following items may be available to constrain the vertical dimensions at each boring location, and the distribution within available borings determine the lateral extent:

- Head space measurements for volatile organics - these will typically show an increase in concentration within the LNAPL zones. Plotting these on a simple chart of depth against concentration will typically show the inferred bulk LNAPL zone (mobile or residual).
- Visual and olfactory comments are typically logged as well, giving another indication of the presence of LNAPL.
- Soil samples are often collected and analyzed chemically, which will give another set of clear LNAPL indications. In general, TPH analytic results (for the appropriate fuel carbon range) greater than 250 mg/kg are indicative of residual LNAPL (because soil has a limited sorbance capacity).
- LNAPL shaker tests of soil samples are also commonly done, and where LNAPL is indicated by sheen or dye tests, that is another delineation point.
- Beyond specific measurements, if one determines an operational source of a release, and the depth of that source is known, then one may easily infer at least the approximate upper extent of that release.

- Fluid gauging hydrographs showing the LNAPL thickness and corrected water table elevation are useful in interpreting the interval affected by free-phase LNAPL as well as the lateral extent of free-phase product.
- The history of groundwater fluctuations over the long-term with respect to the release is also useful. For instance, in many areas, historic refining and terminal operations have experienced wide-ranging hydrologic conditions. Many times those will result in submergence of LNAPL as trapped and often occluded 2-phase residual (recall Figure 7). So although LNAPL is a “floater,” it can be often found at unexpected submergence depths, particularly for older releases or those within a highly dynamic groundwater system.

#### 4.1.7 Assessing LNAPL Migration

As noted above, assessing LNAPL migration is one of the more important aspects of the LCSM. Spreading LNAPL can represent an increasing risk and cleanup footprint, whereas a stable LNAPL plume usually represents a static or decreasing risk scenario (with exceptions). The following site data evaluations provide one way to estimate LNAPL plume migration/stability. A weight of evidence approach is typically necessary to draw conclusions regarding plume mobility.

- Dissolved-phase plume persistence, stability, and mass evaluations can provide an indirect suite of interpretations regarding the LNAPL plume conditions. These approaches are premised on the recognition that LNAPL is the source of the dissolved-phase plume. If the LNAPL is stable, then typically the biodegradable compounds form a stable halo around that source that will contract over time as the source is depleted. To perform these evaluations, the dissolved-phase plume must be adequately delineated and the CoCs of interest must be biodegrading. Most petroleum plumes and compounds fit this constraint, but some such as MTBE and other oxygenates or recalcitrant compounds do not (e.g., PAHs).

These evaluations involve a review of dissolved-phase distribution maps over time along with quantification thereof. Is the geographic footprint of the plume stable or not within some reasonable statistical variation? Has the center of mass of the dissolved-phase plume moved or has it remained stable around the LNAPL source area? Are key CoCs depleting from the plume overall, usually from the outside-in? Within a given volume of groundwater, is there a relevant decrease in mass?

The analysis and evaluations above are straightforward and utilize commonly available site data. There are some associated assumptions one might make for certain plumes, as necessary for the evaluations. Where free product is present in wells that have not been analyzed for dissolved-phase concentrations, it is usually reasonable to approximate those concentrations as being at their effective solubility limits or at the high-range of site data. In cases where the plume boundary may be partly undelineated, one can extend the log-linear concentration profile to estimate that boundary as long as the plume is clearly biodegrading.

A migrating plume will continue to move and disperse for as long as there is a source and/or sufficient mass in the groundwater system.

- LNAPL stability assessment from gauging data is simply a mapping analysis of the LNAPL plume boundaries over time. In particular, one should focus on perimeter locations where LNAPL has not been observed and move inward toward the core of the plume from there. In other words, the lateral boundary and its stability is most important to the assessment. One can look at boring logs or other data points discussed above to ascertain whether LNAPL has been present (mobile or residual) or absent at the mobile phase boundary. LNAPL thickness change with water table variation is common (see discussion above), and that is why the boundary is the focus of this interpretive analysis. If there are any observable trends toward movement, like LNAPL arriving at formerly clean sentry locations or downgradient movement of higher thicknesses, these would be indicative of a mobile plume.
- LNAPL mobility via Darcy's Law flow estimates are also possible using typical site data. The LNAPL gradient may be determined similarly to the groundwater gradient; i.e., by mapping the elevation of the LNAPL/air interface in monitoring wells screened within the same LNAPL body. Note: the LNAPL gradient often differs in both direction and magnitude from the groundwater gradient. The direction of groundwater flow is not always the direction of LNAPL flow, although it exerts some influence.

The effective conductivity with respect to the LNAPL may be estimated in several ways. An LNAPL slug test can be conducted to determine the transmissivity and average conductivity of oil flowing to a particular well or wells (e.g., Huntley, 2000). Saturations can be estimated by the aforementioned TPH conversion calculation (see Equation 2) or through calibrated VEQ estimates, and from that the relative permeability can be calculated. One could also use lab permeability measurement and convert those to conductivity, though it should be noted that discrete lab values are often much smaller than field-scale permeabilities.

With both the gradient and effective conductivity estimated, one would simply use Darcy's Law to estimate an average linear velocity potential of the LNAPL (Equation 7 below). We call it a "potential" because anywhere that LNAPL rebounds into a well and there is a gradient, there will be an estimated degree of movement. However, Darcy's Law does not account for other factors discussed previously that cause the LNAPL plume to come to rest in the subsurface environment. So this approach is a screening method; if the potential velocity is very small, and no other aspects of site data suggest migration, then the weight of evidence would suggest a stable plume.

$$V_p = \frac{K_p \cdot i_p}{(\theta_t \cdot S_p)}$$

(Equation 7) Where  $V_p$  is the average linear pore velocity,  $K_p$  is the effective phase conductivity,  $i_p$  is the phase gradient,  $\theta_t$  is the total porosity and  $S_p$  is the phase saturation.

It is both intuitively and mathematically clear that if either the LNAPL conductivity or gradient are zero (or *de minimis*), there is no LNAPL movement. A threshold for velocity

might be on the order of a landfill liner at  $10^{-6}$  cm/sec, or site-specific values might be developed based on receptor characteristics and a level of inconsequential potential plume movement.

#### 4.1.8 Receptor Identification

Receptors, like the term implies, are any entities that may be in the path of contaminant transport to receive impacts in one or more phases of transport (vapor, water, LNAPL, dust, etc.). Receptors are commonly broken into three categories, with additional subcategories as conditions warrant: 1) Human; 2) Resource, like ground- or surface waters; and 3) Ecological, including other living environments and organisms (other than human) that may be impacted by chemicals emanating from the LNAPL release.

#### 4.1.9 Risk Screening

Risk screening is a method of quantifying the relationships between the source LNAPL, transport pathways, magnitude of impacts at receptors, and the potential health, resource or ecological risk associated with those chemical arrivals. Risk screening typically considers both timing, magnitude, and duration of potential threats. For instance, a small LNAPL release may pose a short-term threat to nearby receptors, but because of its limited mass may not pose a long-term threat. Conversely, a large stable LNAPL release may pose no threats today under existing land-use conditions, but could pose a future threat if those land-use and receptor conditions change.

As noted, the HDOH accepts validated risk screening and risk assessment methods, such as the EPA Risk Assessment Guidelines for Superfund Sites, and the ASTM Risk-based Corrective Action Methodology. Both are similar in quantifying specific risks based on transport, toxicity, hazard, and other factors that combined result in a quantification of risk. Both methods begin with limiting and conservative assumptions that produce worst-case risk potentials, and allow for further refinements as data and results warrant. This parallels precisely the drivers for advancing LCSMs from Tier I to more advanced Tiers.

## 4.2 SUMMARY OF THE LCSM

The LCSM is simply a summary of the inter-linked conditions and considerations that ultimately drive risk for any particular site. The thought and interpretive process necessary to construct the LCSM is what elucidates data gaps and uncertainties. Simply, if there is a facet of the LCSM that cannot be answered with existing data, and that facet is important, then additional data collection and/or evaluations would be suggested.

The HDOH strongly favors the use of all existing site data as a starting point before considering recommendations for additional data collection. And while multiphase and multicomponent modeling can assist in clarifying the meaning of site data, an emphasis on data is favored. Modeling that does not represent actual site data will typically be of little value.

## GLOSSARY

Term &/or Abbreviation	Definition
Brooks-Corey Sorting Index (8); unitless	A capillary characteristic curve fitting parameters roughly proportional to the pore size sorting (high values, good pore sorting and low pore size variability).
Brooks-Corey Bubbling Pressure Head (Pd); length	A capillary characteristic curve fitting parameters proportional to the theoretical entry pressure head for air to begin to displace water in the pore space.
Bulk density ( $D_b$ ) (mass/volume)	The dry density of soil, or the mass of a material divided by its volume. The bulk density includes the negligible weight of air in the pore space.
Capillarity	The characteristic rise of a wetting fluid due to surface tension in small pores. This is the most sensitive parameter set for smear zone issues and fuel recovery. The capillary characteristic curve of a soil is the representation of the wetting phase retention as a function of capillary pressure between 2 phases (e.g., water-air, oil-water, air-oil).
Conductivity (K); length/time	A measure of the discrete capacity of a geologic material to conduct a specific fluid. Coarse granular materials generally have high conductivity, and fine materials small values.
Darcy Velocity (q); length/time	The specific discharge, or volumetric discharge per unit area of groundwater flow through a porous material.
DNAPL	Dense non-aqueous phase liquid, a compound that is relatively immiscible with water and more dense.
Effective solubility	The maximum solubility of a specific compound in a multicomponent mixture based on its pure phase solubility and its molar fraction in the mixture.
Effective Transmissivity ( $T_e$ ); length <sup>2</sup> /time	The vertical integral of $K_e$ and a measure of the relative flow or recovery capacity of a particular fluid under a specific saturation condition.
Effective Conductivity ( $K_e$ ); length/time	The product ( $k_i \parallel k_r Dg/ \cdot$ ) for any phase, water, vapor, fuel, or other NAPL, where D is the fluid phase density, $\cdot$ is the fluid phase viscosity, and g is gravitational acceleration.

Grain density ( $D_s$ )	The density of soil grains, or the mass of the granular material divided by its volume. For many sediments, the grain density is close to 2.65 g/cc reflecting quartz-rich composition.
Groundwater Gradient (i)	The change in groundwater potential (head) from one point to another, usually measured as horizontal and vertical components. Groundwater flows downgradient.
Intrinsic Permeability ( $k_i$ ); length <sup>2</sup>	Related to conductivity, permeability is a measure of a geologic material's intrinsic capacity to transmit any fluid.
Leakance (r/B)	<i>Proportional to vertical fluid flow in a system with leaky geologic units (vapor or water). A value of zero implies perfectly radial flow (no vertical component), with increasing values indicating greater vertical components.</i>
Linear Pore Velocity ( $q_p$ , $v_p$ ); length/time	The averaged linear flow rate of fluids through the pore space, $v/n$ , which accounts for the fact that fluids move only through matrix voids (pore space) and not solids. The average linear flow rate is always greater than the specific discharge.
LIF	Laser-Induced Fluorescence
LNAPL	Light non-aqueous phase liquid that is relatively immiscible with water and less dense (typically oils).
Mass content (M)	The mass of fluid divided by the mass of soil. This unit is often used in geotechnical measurements.
Multicomponent	Refers to mixtures composed of hundreds of individual compounds at varying molar fractions, such as in most fuels.
Porosity (n)	The volume of matrix voids divided by the total matrix volume.
Relative Permeability ( $k_r$ ); unitless	A scalar from 0 to 1.0 that reflects the relative ability of a fluid to move under variably saturated conditions. A key parameter in multiphase evaluations of the smear zone and related remediation options.

Residual saturation ( $S_r$ )	The saturation threshold below which no further hydraulic movement is possible under any gradient and remaining fluids (water, NAPL, air) are present but in disconnected pore spaces. This is essentially a lower limit to phase mobility, and varies between 2-phase and 3-phase conditions.
Saturation ( $S$ )	Fraction of the pore space occupied by a given fluid, usually expresses as a value between 0.0 and 1.0. Concentration units can be converted to saturation if the fluid and bulk density is known.
Transmissivity ( $T$ ); length <sup>2</sup> /time	The vertical integral of hydraulic conductivity across an aquifer section, and a measure of the total flow capacity of that aquifer section for a given head drop.
Wetting Fluid	The fluid that has the greatest affinity for the pore space walls and occupies the pore space adjacent to those walls under all conditions but in varying saturations. In most conditions the wetting fluid is water.
Non-wetting Fluid	A fluid in the pore space that has secondary affinity for the pore space walls and resides within the wetting fluid space and is typically found in the larger pore spaces within a given matrix.
Van Genuchten alpha ( $\alpha$ ); 1/length	A capillary characteristic curve fitting parameters inversely proportional to the capillary rise (high values, low rise & greater pore diameters).
Van Genuchten beta ( $\beta$ ); unitless (sometimes denoted as "n")	A capillary characteristic curve fitting parameters roughly proportional to the pore size sorting (high values, good pore sorting and low pore size variability).
Viscosity, centipoise (cp)	The dynamic viscosity is a measure of the internal shear resistance of a fluid. Low viscosity fluids flow more easily than high viscosity liquids.
Volumetric content ( $\theta$ )	The volume of fluid divided by the volume of soil. The maximum volumetric content is equal to the porosity.
scfm	Standard cubic feet per minute, usually referring to vapor recovery/injection rates.
gpm, gph, gpd	Gallons per minute (m), hour (h), day (d), usually referring to liquid recovery/injection rates.

Psia	Pounds per square inch against atmospheric
in Hg, iw	Pressure or vacuum in equivalent head units, inches mercury, inches water.
lbs	Pounds.
kg, g, mg, ug	Kilogram, gram, milligram, microgram.
m, cm, mm, um	meter, centimeter, millimeter, micrometer.
yd, ft, in	yard, foot, inch.
l	liter.
mg/kg	milligrams per kilogram, parts per million (ppm) by mass for soil.
ug/kg	micrograms per kilogram, parts per billion (ppb) by mass for soil.
mg/l	milligrams per liter, parts per million (ppm) by mass equivalent for water, but not vapor.
ug/l	micrograms per liter, parts per million (ppm) by mass equivalent for water, but not vapor.
ppmv	part per million by volume, usually used for vapor phase concentrations.
ppbv	part per billion by volume, usually used for vapor phase concentrations.
COC	Compounds of concern from a regulatory, health, or environmental safety perspective.
MCL	Maximum contaminant level; a regulatory compliance threshold applicable to certain contaminants in certain environments.
TPH	Total petroleum hydrocarbons, usually a mass integral of various compounds in fuels within a specified range based on the preparation and analytic technique. TPH_g, TPH_d are typically used to designate gasoline and diesel range TPH values.
TBA	Tertiary butyl-alcohol; an impurity in MTBE and also a biodecay daughter product of MTBE degradation. TBA is fully soluble, transportable, and is generally less amenable to biodegradation than other fuel compounds.

TAME	Tertiary amyl methyl ether, an oxygenated fuel additive.
MTBE	Methyl tertiary butyl ether, an oxygenated fuel additive. MTBE is highly soluble, transportable, and is generally less amenable to biodegradation than other fuel compounds.
BTEX	The abbreviation of the typical common aromatic hydrocarbons of concern; benzene, toluene, ethyl benzene, and xylene isomers.
Gro	Gasoline range organics.
Dro	Diesel range organics.
PVC	Polyvinyl chloride plastic
HDPE	High density polyethylene plastic
USGS	United States Geological Survey
EPA	Federal Environmental Protection Agency
HEER	Hazard Evaluation and Emergency Response Office
HDOH	State of Hawai'i Department of Health

**BIBLIOGRAPHY**

Abriola, L.M. and Pinder, G.F., 1985b. A Multiphase Approach to the Modeling of Porous Media Contamination by Organic Compounds, 2. Numerical Simulation. *Water Resources Res.*, Vol. 21, No. 1, pp. 19-26.

Abriola, L.M. and Pinder, G.F., 1985a. A Multiphase Approach to the Modeling of Porous Media Contamination by Organic Compounds, 1. Equation Development. *Water Resources Res.*, Vol. 21, No. 1, pp. 11-18.

American Petroleum Institute - API Interactive LNAPL Guide, 2004 ([www.api.org/lnapl](http://www.api.org/lnapl)).

API, "Evaluation of Sampling and Analytical Methods for Measuring Indicators of Intrinsic Bioremediation," *Soil & Groundwater Research Bulletin*, No. 5, American Petroleum Institute, 1998.

Anderson, K. S., Brearly, M., Widness, S. E., Cook, D. A., and Baird, B., "A Guide to the Assessment and Remediation of Underground Petroleum Releases, 3rd Edition," API Publication 1628, American Petroleum Institute, 1996.

ASTM E2530-06, 2006. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface.

ASTM 1943-98, 1998. Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites.

Baehr, A.L., 1987. Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning. *Water Resources Res.*, Vol. 23, No.10, pp. 1926-1938.

Beahr, A.L. and Corapcioglu, M.Y., 1987. A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products, 2. Numerical Solution. *Water Resources Res.*, Vol 23, No. 1, pp. 201-214.

Beckett, G.D., Lundegard, P., 1997. Practically Impractical - The Limits Of LNAPL Recovery And Relationship To Risk. *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, Houston

Beckett, G.D., Huntley, D., 1994, The Effect of Soil Characteristics on Free-Phase Hydrocarbon Recovery Rates. *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, Houston

Beckett, G. D., Huntley, D., 1998. Soil Properties and Design Factors Influencing Free-Phase Hydrocarbon Cleanup, *Environmental Science & Technology*, 32(2); 287-293.

Blake, S.B., and Hall, R.A., 1984. Monitoring Petroleum Spills with Wells; Some Problems and Solutions. Proceedings of the Fourth National Symposium on Aquifer Restoration and Ground Water Monitoring, National Water Well Association.

Brian Murphy & Robert Morrison (ed). Introduction to Environmental Forensics, 2nd Edition, March 2007. Elsevier.

Barcelona, M. J., Fang, J., and West, C., "Monitoring In Situ Bioremediation of Fuel Hydrocarbons—The Use of Chemical and Biogeochemical Markers," Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, National Groundwater Association/API, Houston, TX, 1996.

Brooks, R.H. and Corey, A.T., 1964. Hydraulic Properties of Porous Media. Colo. State Univ., Fort Collins, Colo., Hydrol. Pap. No. 3, pp. 27.

Burdine 1953. Relative Permeability Calculations from Pore-Size Data. Trans A.I.M.E. 198, p 71-77.

Buscheck, T. E., Wickland, D., and Kuehne, D., "Multiple Lines of Evidence to Demonstrate Natural Attenuation of Petroleum Hydrocarbons," Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National GroundWater Association/API, Houston, TX, 1996.

Charbeneau et al., 1999. Free Product Recovery of Liquid Hydrocarbons, API Publication #4682, Health and Environmental Sciences Department of the American Petroleum Institute.

Charbeneau, R. J., "Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids," API Publication 4729, American Petroleum Institute, Washington, D.C., 2003.

Clapp, R. B., and Hornberger, G. M., "Empirical Equations for Some Soil Hydraulic Properties," Water Resources Research, Vol 14, No. 4, 1978, pp. 601–604.

Cohen, Andrew J.B. et al, 1996. Hydrogeologic Characterization of Fractured Rock Formations: A Guide for Groundwater Remediators. Summary report.

Cohen, Andrew J.B. , 1995. Hydrogeologic Characterization of Fractured Rock Formations: A Guide for Groundwater Remediators. Full report.

Corapcioglu, M.Y. and Beahr, A.L., 1987. A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products, 1. Theoretical Considerations. Water Resources Res., Vol. 23, No. 1, pp. 191-200.

Corey, A.T., 1986. Mechanics of Immiscible Fluids in Porous Media. Water Resources Publications, Littleton, Colo., pp. 259.

Daniel J. Goode, Thomas E. Imbrigiotta & Pierre J. Lacombe, 2014. High-resolution delineation of chlorinated volatile organic compounds in a dipping, fractured mudstone: Depth- and strata-dependent spatial variability from rock-core sampling.

Davis, S. N., "Porosity and Permeability of Natural Materials," Flow Through Porous Media, R. J. M. De Wiest, ed., Academic Press, New York, NY, 1969.

Delshad, M. and Pope, G.A., 1989. Comparison of the Three-phase Oil Relative Permeability Models. *Transp. Porous Media*, Vol. 4, No.1, pp. 59-83.

Douglas, G.S., Emsbo-Mattingly, S.D., Stout, S.A., Uhler, A.D., and McCarthy, K.J. (2015). Hydrocarbon fingerprinting methods. In: *Introduction to Environmental Forensics*, 3rd Ed., B. Murphy and R. Morrison, Eds., Academic Press, New York, pp. 201-310.

Driscoll, F.G., 1986. *Ground water and wells*, Second Edition. Johnson Filtration Systems Inc., St. Paul, Minnesota

EPA 542-R-04-011, 2005. A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL).

F. L. Paillet & D. M. Thomas, 1996. Hydrogeology of the Hawaii Scientific Drilling Project Borehole KP-1: 1. Hydraulic conditions adjacent to the well bore.

Farr, A.M., Houghtalen, R.J. and McWhorter, D.B., 1990. Volume Estimates of Light Nonaqueous Phase Liquids in Porous Media. *Ground Water*, Vol. 28, No.1, pp. 48-56.

Faust, C.R., 1985. Transport of Immiscible Fluids Within and below the Unsaturated Zone: a Numerical Model. *Water Resources Res.*, Vol. 21, No. 4, pp. 587-596.

Ferrand, L.A., Milly, P.C.D. and Pinder, G.F., 1989. Experimental Determination of Three-fluid Saturation Profiles in Porous Media. *J. Contam. Hydrol.*, Vol. 4, No. 4, pp. 373-395.

Fetter, C.W., 1994. *Applied Hydrogeology*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Forsyth, P.A., 1990. A Finite Volume Approach to LNAPL Groundwater Contamination, Research Report, CS-89-46. University of Waterloo, Waterloo, Ontario, Canada.

Freeze, R.A., and J.A. Cherry., 1979. *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Gillham, R.W., Klute, A. and Heermann, D.F., 1979. Measurement and Numerical Simulation of Hysteretic Flow in a Heterogeneous Porous Media. *Soil Sci. Soc. J.*, Vol. 43, pp. 1061

Hillel, D., 1980. *Introduction to soil physics*. Academic Press, Inc. San Diego, California, 92101.

Hoag, G.E. and Marley, M.C., 1986. Gasoline Residual Saturation in Unsaturated Uniform Aquifer Materials. *J. Environ. Eng., Proc. Am. Soc. Civ. Eng.*, Vol. 112, No. 13, pp. 586-604.

Honapour, M. and Mahmood, S.M., 1988. Relative-permeability Measurements: an Overview. *J. Pet. Technol.*, Vol. 40, No. 8, pp. 963-966.

Howard, P. H., *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Volumes 1 and 2, Lewis Publishers, Chelsea, MI, 1989.

Hunt, J.R., Sitar, N. And Udell, K.S., 1988a. Nonaqueous Phase Liquid Transport and Cleanup, 1. Analysis of Mechanisms. *Water Resources Res.*, Vol. 24, No. 8, pp. 1247-1258.

Hunt, J.R., Sitar, N. And Udell, K.S., 1988b. Nonaqueous Phase Liquid Transport and Cleanup, 2. Experimental Studies. *Water Resources Res.*, Vol. 24, No. 8, pp. 1259-1269.

Huntley, D., Beckett, G.D., 2002. American Petroleum Institute Publication #4715. Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Magnitude.

Huntley, D., 1997. Analytic Determination of Hydrocarbon Transmissibility from Baildown Tests. Conference Proceedings of the 1997 Petroleum Hydrocarbons & Organic Chemicals in Ground Water. Houston, Texas, sponsored by the National Ground Water Association & American Petroleum Institute.

Huntley, David, 2006. Draft Investigation of Hydrocarbon, OU1C, Honolulu Harbor. February 22.

Huntley, D., Hawk, R.N., and Corley, H.P., 1994. Non-aqueous Phase Hydrocarbon in a Fine-Grained Sandstone, (1) Comparison Between Measured and Predicted in Saturations and Mobility: *Journal of Ground Water*

Huntley, D., Hawk, R.N., and Corley, H.P., 1994, Non-aqueous Phase Hydrocarbon in a Fine-grained Sandstone, (1) Comparison Between Measured and Predicted Saturations and Mobility: *Journal of Ground Water*, v. 32, n. 4.

Huntley, D., Beckett, G.D., 2002. Persistence of LNAPL Sources: Relationship Between Risk Reduction and LNAPL Recovery. *Journal of Contaminant Hydrology*, #59, pp 3 - 26. Revised 1997 NGWA Conference manuscript.

Huntley, D., Hawk, R., and Wallace, J., 1991, an Analysis of the History, Distribution, and Movement of the Blob, a Hydrocarbon Pool Underlying Downtown San Diego; in, Abbott, P. (ed), *Environmental Perils: San Diego Association of Geologists*.

Huyakorn, P.S., Wu, Y.S. and Park N.S., 1994. An Improved Sharp-interface Model for Assessing LNAPL Contamination and Remediation of Groundwater Systems. *Journal of Contaminant Hydrology*, Vol. 16, pp. 203-234.

Huyakorn, P.S., Panday, S., and Wu, Y.S., 1994. A Three-dimensional Multiphase Flow Model for Assessing LNAPL Contamination in Porous and Fractured Media: I. Formulation. *Journal of Contaminant Hydrology*, Vol. 16, pp 109-130.

Interstate Technology Regulatory Council, 2009. *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*.

Environment Canada Oil Properties Database: <http://www.etc-cte.ec.gc.ca/databases/oilproperties/>

Stout, S.A., Douglas, G.S., and Uhler, A.D. (2016). Chemical fingerprinting of gasoline and distillate fuels. In: *Standard Handbook of Oil Spill Environmental Forensics: Fingerprinting and Source Identification*, 2nd Ed., S.A. Stout and Z. Wang, Eds., Elsevier Publishing Co., Boston, MA, p. 509-564.

Kienhuis, P.G.M., Hansen, A.B., Faksness, L.-G., Stout, S.A., and Dahlmann, G. (2016). CEN methodology for oil spill identification. In: *Standard Handbook of Oil Spill Environmental Forensics: Fingerprinting and Source Identification*, 2nd Ed., S.A.

Kruseman, G.P., and N.A. DeRidder, 1979. Analysis and Evaluation of Pumping Test Data, Bulletin 11, International Institute for Land Reclamation and Improvements, Wageningen, Netherlands, p. 200.

L.M. Gibbs, "How Gasoline Has Changed", SAE Technical Paper Series - 932828, International Fuels and Lubricants Meeting & Exposition, Philadelphia, Pennsylvania, October 18-21, 1993

Lenhard, R.J., and Parker, J.C., 1990. Estimation of Free Hydrocarbon Volume from Fluid Levels in Monitoring Wells. *Ground Water*, v. 28, no.1, p. 57-67.

Lenhard, R.J. and Parker, J.C., 1988. Experimental Validation of the Theory of Extending Two-phase Saturation - Pressure Relations to Three-fluid Phase Systems for Monotonic Drainage Paths. *Water Resources Res.*, Vol. 24, No. 3, pp. 373-380.

Lundegard, P.D., Mudford, B., 1995. A Modified Approach to Free Product Volume Estimation. Conference Proceedings of the 1997 Petroleum Hydrocarbons & Organic Chemicals in Ground Water. Houston, Texas, sponsored by the National Ground Water Association & American Petroleum Institute.

MAGNAS3, 1992, 1994. *Multiphase Analysis of Groundwater, Non-aqueous Phase Liquid and Soluble Component in 3 Dimensions. Documentation and User's Guide*, Hydrogeologic, Inc., Herndon, Virginia.

McDonald, M.G., and Harbaugh, A.W., 1988. A Modular Three-Dimensional Finite Difference Ground-Water Flow Model: U.S. Geological Survey Techniques of Water-Resources Investigations Book 6, Chapter A1.

Mercer, J.W., Faust, C.R., Cohen, R.M., Andersen, P.F. and Huyakorn, P.S., 1985. Remedial Action Assessment for Hazardous Waste Sites via Numerical Simulation. *Water Man. Res.*, 3, pp. 377-387.

Mercer, J.W., and Cohen, R.M., 1990. A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation. *Journal of Contaminant Hydrology*, Vol. 6, Pp. 107-163.

Morrow, N.R., Chatzis, I. and Taber, J.J., 1988. Entrapment and Mobilization of Residual Oil in Bead Packs. *Soc. Pet. Eng. Reserv. Eng.*, Aug. 1988, Pp. 927-934.

Mualem, Y., 1976a. A Catalogue of the Hydraulic Properties of Unsaturated Soils. Development of Methods, Tools and Solutions for Unsaturated Flow with Application to Watershed Hydrology and Other Fields. Israel Institute of Technology.

Mualem, Y., 1976b. A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media. *Water Resources Research*. Volume 12, pp. 513-522.

Neuman, S.P., 1975. Analysis of Pumping Data from Anisotropic Unconfined Aquifers Considering Delayed Gravity Response. *Water Resources Research*, 11(2), pp. 329-342.

Nilkuha, K. and Huyakorn, P., 1989. Numerical Solution of Two-phase Flow Through Porous Media, Dept. Of Geoscience, New Mexico Inst. Of Mining and Technology.

Ostendorf, D.W., 1990. Long Term Fate and Transport of Immiscible Aviation Gasoline in the Subsurface Environment. *Water Science and Technology*, Vol. 22, pp. 37-44.

Panday, S., Forsyth, P.A., Falta, R.W., Wu, Y.S. and Huyakorn, P.S., 1995. Considerations for Robust Compositional Simulations of Subsurface Nonaqueous Phase Liquid Contamination and Remediation. *WRR*, Vol. 31, No. 5, pp. 1273-1289.

Panday, S., Wu, Y.S., Huyakorn, P.S., and Springer, E.P., 1994. A Three-dimensional Multiphase Flow Model for Assessing LNAPL Contamination in Porous and Fractured Media: Ii. Porous Medium Simulation Examples. *Journal of Contaminant Hydrology*, Vol 15, pp 131-156.

Pankow, J.F., Cherry, J.A., 1996. Dense Chlorinated Solvents and Other DNAPLs in Groundwater. Waterloo Press, Portland, Oregon..

Peaceman, D.W., 1977. Fundamentals of numerical reservoir simulation. Elsevier, Amsterdam, pp. 176.

Pinder, G.F. and Abriola, L.M., 1986. On the Simulation of Nonaqueous Phase Organic Compounds in the Subsurface. *Water Reserv. Res.*, Vol. 22, No. 9, pp. 109S-119S.

Rathmell, J.J., Braun, P.H. and Perkins, T.K., 1973. Reservoir Waterflood Residual Oil Saturation from Laboratory Tests. *J. Pet. Technol.*, pp. 175-185.

Schiegg, H.O., 1985. Considerations on Water, Oil, and Air in Porous Media. *Water Science Technol.*, Vol. 23, No. 4 & 5, pp. 467-476.

Stone, H.L., 1973. Estimation of Three-phase Relative Permeability and Residual Oil Data. *Can. Pet. Technol.*, Vol. 12, No. 4, pp. 53-61.

Stout, S.A. and Wang, Z. (2016). Chemical fingerprinting methods and factors affecting petroleum fingerprints in the environment. In: *Standard Handbook of Oil Spill Environmental Forensics: Fingerprinting and Source Identification*, 2nd Ed., S.A. Stout and Z. Wang, Eds., Elsevier Publishing Co., Boston, MA, p. 61-130.

Theis, C.V., 1935. The Relation Between the Lowering of the Piezometric Surface and the Rate and Duration of Discharge of a Well Using Ground Water Storage. *American Geophysical union Transactions*, vol. 16, pp. 519-524.

van Genuchten, M.Th., 1980. A Closed Form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils. *Soil Sci. Soc. Am. J.* 44, pp.892-898.

Wise, W.R., Chang, C.C., Klopp, R.A. and Bedient, P.B., 1991. Impact of Recharge Through Residual Oil upon Sampling of Underlying Ground Water. *GWMR*, pp. 93-99.

Wu, Y.S., Huyakorn, P.S. and Park, N.S., 1994. A Vertical Equilibrium Model for Assessing Nonaqueous Phase Liquid Contamination and Remediation of Groundwater Systems. *WRR*, Vol. 30, No. 4, pp. 903-912.



**APPENDIX A**  
**PARAMETERS AFFECTING LNAPL CONDITIONS**

**TABLE 1  
LCSM PARAMETERS AND CONDITIONS**

**General Site Conditions**

<b>Parameter/Factor</b>	<b>Potential Sources</b>	<b>Sensitivity</b>	<b>How to Determine</b>
1 Site Layout and Use	Site specific	Site dependent	Mapping from as-built plans, aerial photos, etc.
2 Historic LNAPL Infrastructure	Site specific	Site dependent	Mapping from as-built plans, aerial photos, etc.
3 Subsurface Utilities/Conduits	Site specific	Site dependent	Mapping from as-built plans, state/county records.
4 Release Sources	Site specific	Site dependent	Characterization data to determine likely sources. Literature review for other area sources.
5 Local/Area Land-use & Zoning	Area specific literature	Site dependent	Area reconnaissance, aerial mapping, zoning, and other resources.
5 Potential Human Receptors	Site and area specific	Site dependent	Review of land use conditions within potential zone of contaminant impacts
6 Potential Resource Receptors	Site and area specific	Site dependent	Review of resource use conditions within potential zone of contaminant impacts
7 Potential Ecological Receptors	Site and area specific	Site dependent	Review of ecological setting with potential zone of contaminant impacts, augmented by literature studies.

**Hydrogeology**

<b>Parameter/Factor</b>	<b>Potential Sources</b>	<b>Sensitivity</b>	<b>How to Determine</b>
1 Hydrostratigraphy	Site specific	Variable, depending on conditions and complexity	Site specific data and interpretation, potential reliance on area studies.
2 Depth to groundwater	Site specific	Mostly related to vapor pathway, important when receptors overlie the plume.	Site specific data and investigation.
3 Groundwater gradient	Site specific	Site dependent	Site specific data and interpretation, potential reliance on area studies.
4 LNAPL gradient	Site specific	Site dependent	Site specific data and interpretation.
4 Recharge areas	Locality specific	Site dependent	Site specific data and interpretation, potential reliance on area studies.
5 Discharge areas	Locality specific	Site dependent	Site specific data and interpretation, potential reliance on area studies.
6 Plume distribution in all phases	Site specific	Typically important	Site specific data and interpretation.
7 Area hydrologic conditions	Area specific literature	Site dependent	

**Aquifer/Matrix Parameters**

<b>Parameter/Factor</b>	<b>Potential Sources</b>	<b>Sensitivity</b>	<b>How to Determine</b>
1 Capillarity and hysteresis	Site-specific preferred, or literature values as screening	High (nonlinear)	Coring with standard lab testing, capillary parameters fit to data.
2 Intrinsic permeability & Conductivity	Site-specific preferred, or literature values as screening	Medium (linear)	Aquifer pump, slug, or other subsurface in situ testing typically most reliable. Coring and petrophysical lab testing.
3 Relative permeability	Site-specific or literature values	High (nonlinear)	Coring and petrophysical lab tests, model fits to field data, or assumed from literature values.
4 Porosity	Site-specific or literature values	Low (except fractured conditions)	Coring with standard lab testing or estimated from literature values.
5 Residual fluid saturation	Site-specific or literature values	High (variable value depending on)	Fluid sampling with lab testing. LNAPL 2-phase and 3-phase residuals most important.
6 Dry bulk density	Site-specific or literature values	Low	Coring with standard lab testing or estimated from literature values.
7 Grain density	Site-specific or literature values	Low	Coring with standard lab testing or estimated from literature values.
8 Grain size distribution	Site specific	Low, used for cross-correlations	Coring with standard lab testing.
9			
10 Matrix compressibility	Site-specific or literature values	Low	Aquifer pump testing typically most reliable. Coring and petrophysical lab testing.

### Fluid Properties

<b>Parameter/Factor</b>	<b>Potential Sources</b>	<b>Sensitivity</b>	<b>How to Determine</b>
1 Interfacial fluid tensions	Site-specific or literature values	High (nonlinear). All 3 IFT couplets can vary depending on release age/conditions.	Fluid sampling with lab testing.
2 Liquid density	Site-specific or literature values	Medium. LNAPL density most important, water and air well defined in literature.	Fluid sampling with lab testing.
3 Viscosity	Site-specific or literature values	Medium (linear). LNAPL viscosity most important, water and air well defined in literature.	Fluid sampling with lab testing.

4 Fluid Compressibility

Literature values

Low

Fluid sampling with standard lab testing

**Fate and Transport Properties**

1 Dispersivity, 3 Dimensions

Site-specific or literature values

Medium

Field scale fit of transport modeling is best, supported by literature.

2 Tortuosity

Literature values

Medium

Estimation from site analytic data or lab testing.

3 Molar fractionation of chemicals

Site-specific or literature values

Medium

4 Molecular diffusion coefficients

Literature values

Low

Field scale fit of transport modeling is best, supported by

5 Biodegradation decay rates

Site-specific or literature values

High (controls flux/risk of the dissolved-

literature.

6 Soil sorbance factors

Site-specific or literature values

Low

Estimate from organic carbon content

7 Henry's coefficient

Literature value

Medium

8 Raoult's coefficient

Literature value

Medium

9 Solubility coefficient

Literature value

Medium

10 Total organic carbon

Site-specific or literature values

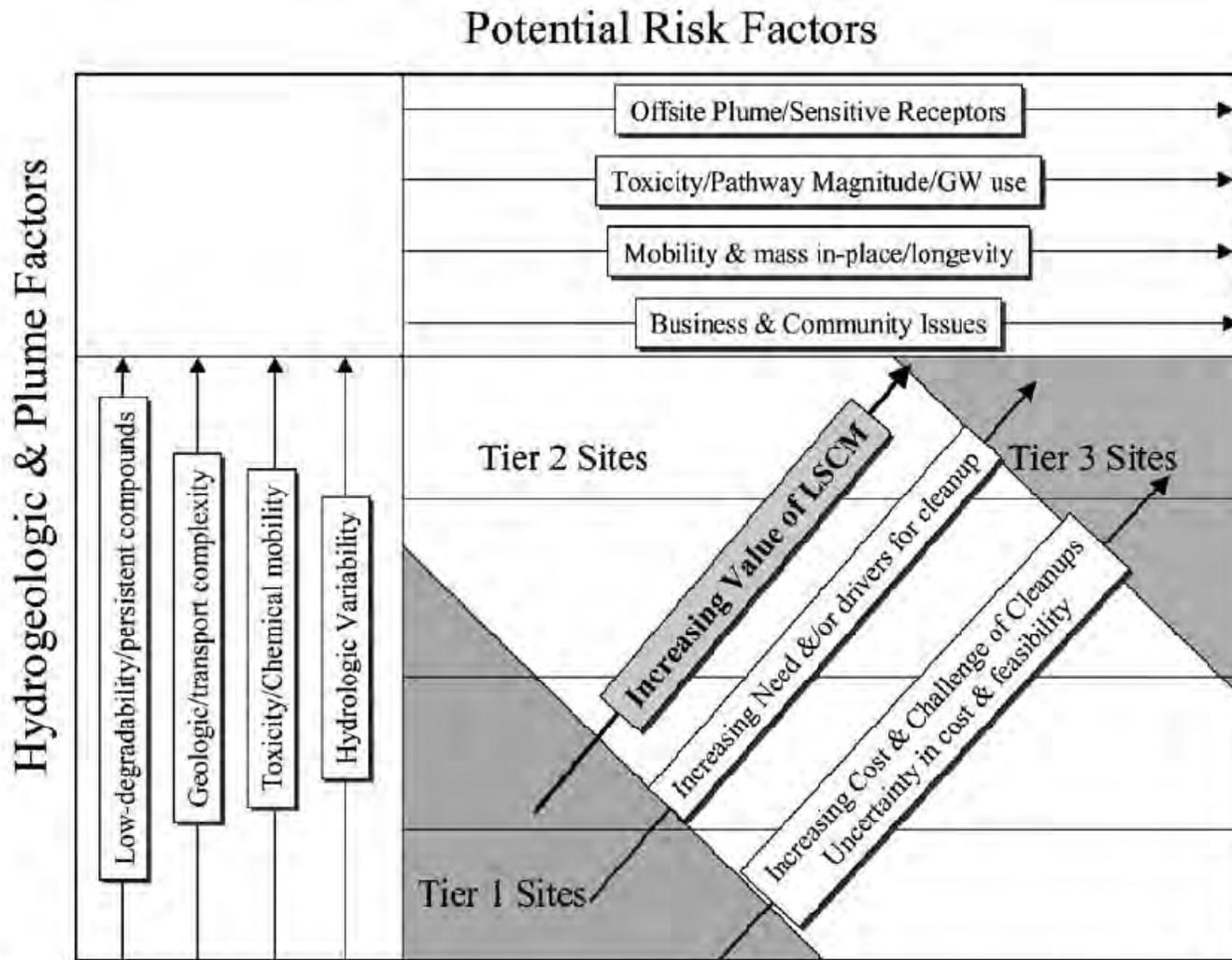
Low, affects dissolved-phase retardation.

Coring with standard lab testing or estimated from literature

# Figures

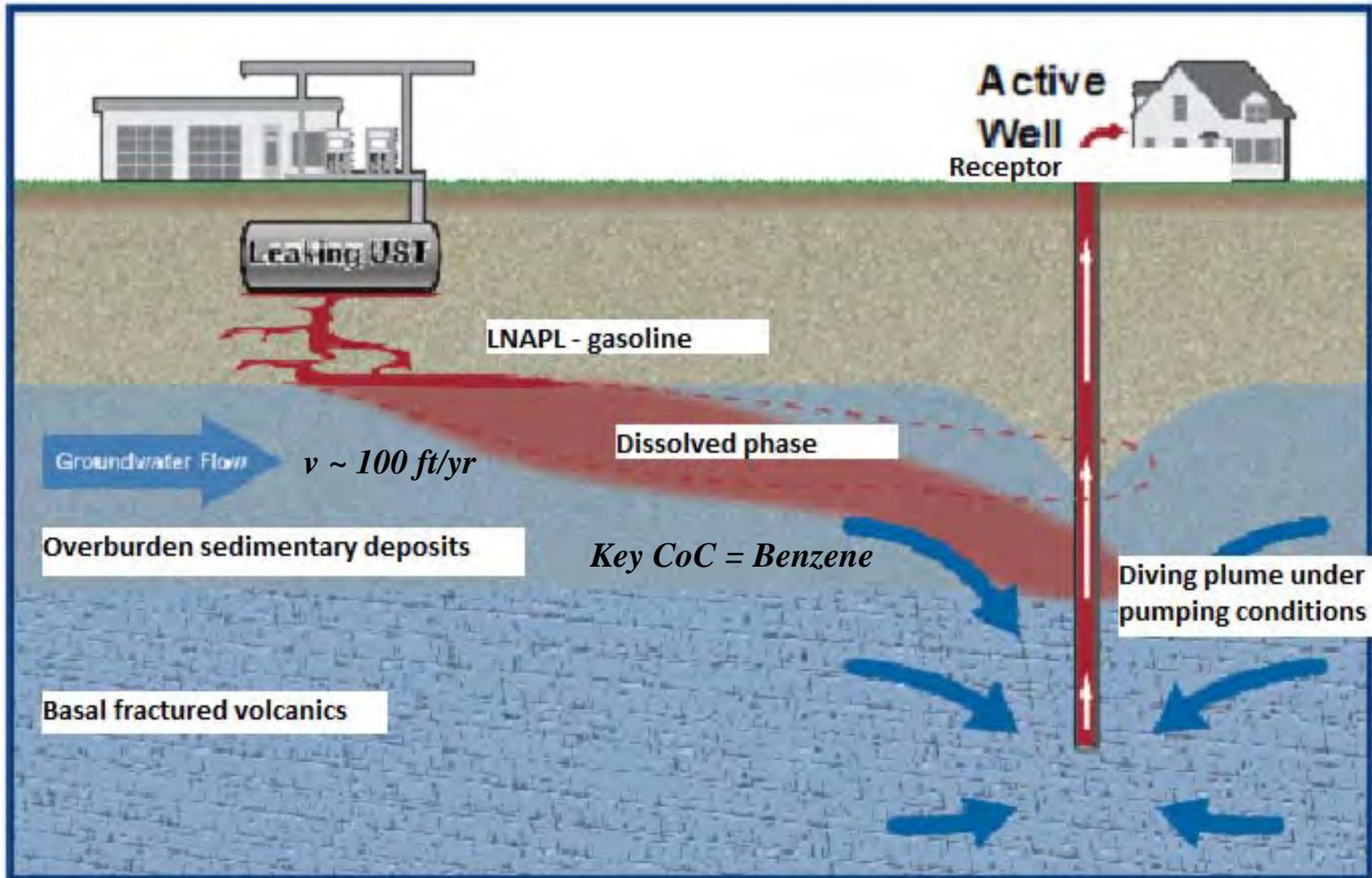


# Figure 1

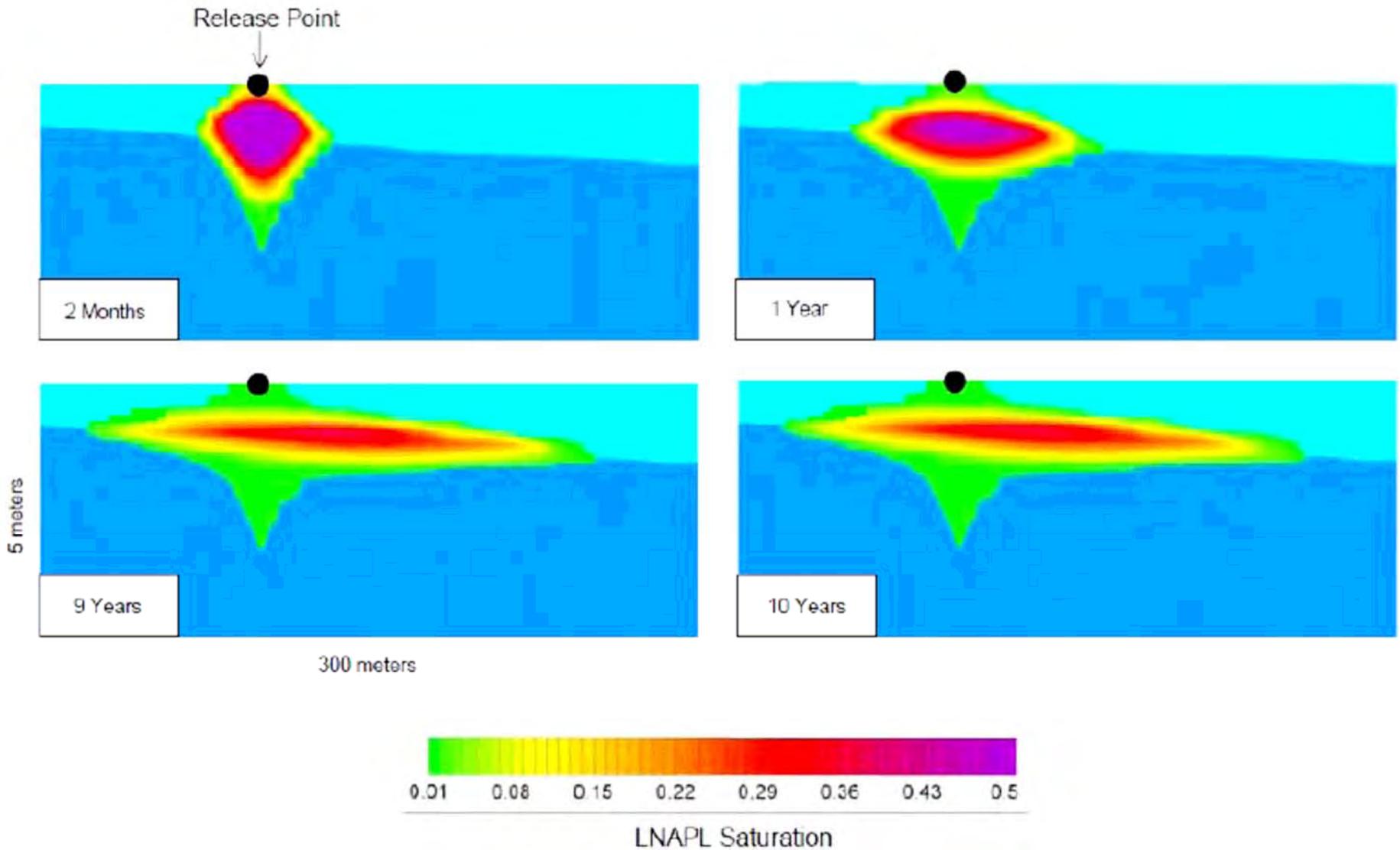


**Figure 1** - Relative Complexity and Value of the LNAPL Conceptual Site Model (CSM). Concept after Tom Sale, 2002.

Figure 2: Example Tier I LCSM Graphic  
(note, only part of the total LCSM)

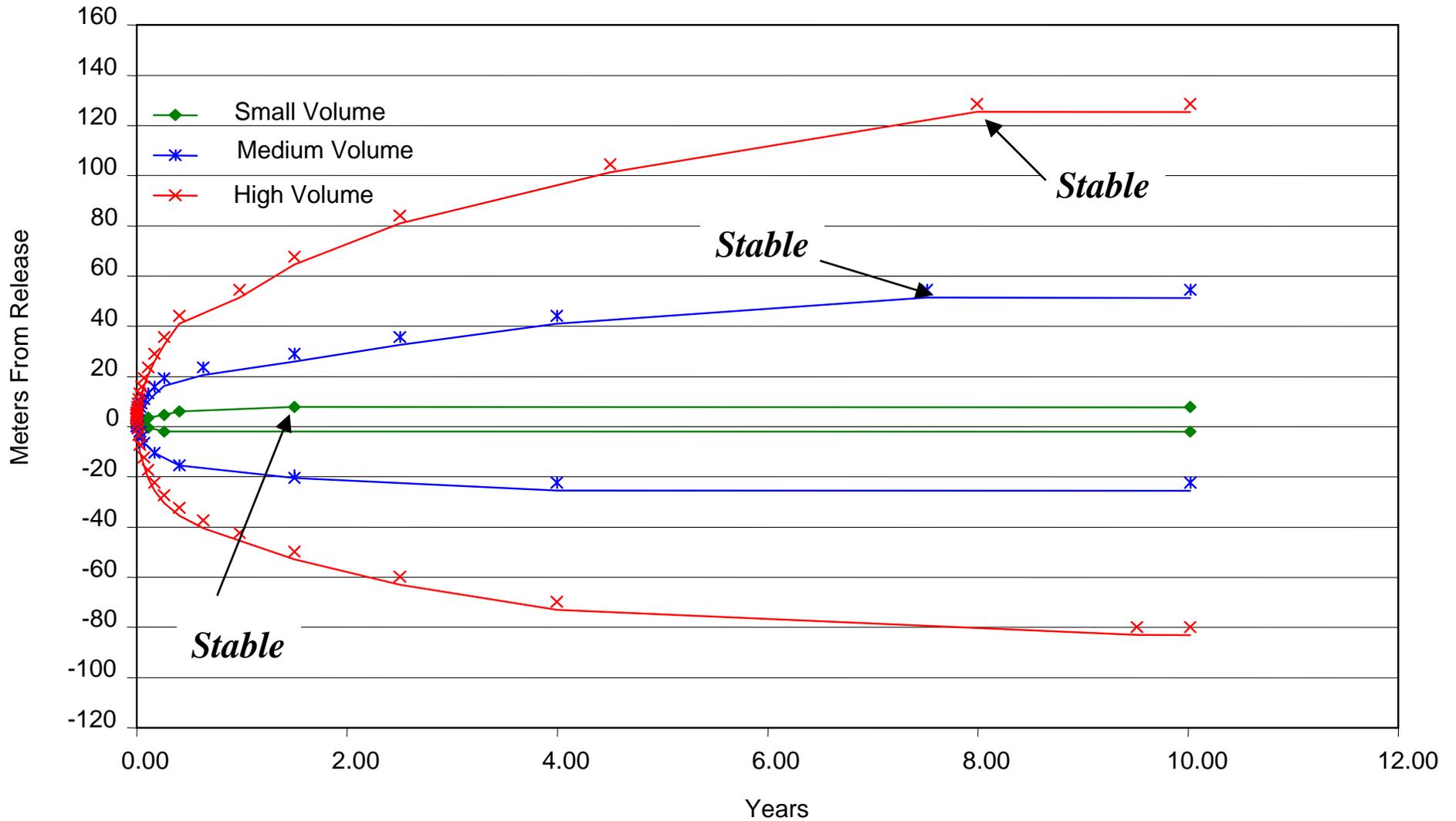


# Figure 3: Generalized LNAPL Plume Genesis



# Figure 4: LNAPL Migration Through Time

*(high permeability soil, gasoline released over one month)*



# Figure 5: Soil Capillary Characteristic Curves

*For Five Progressively Coarser Soil Types*

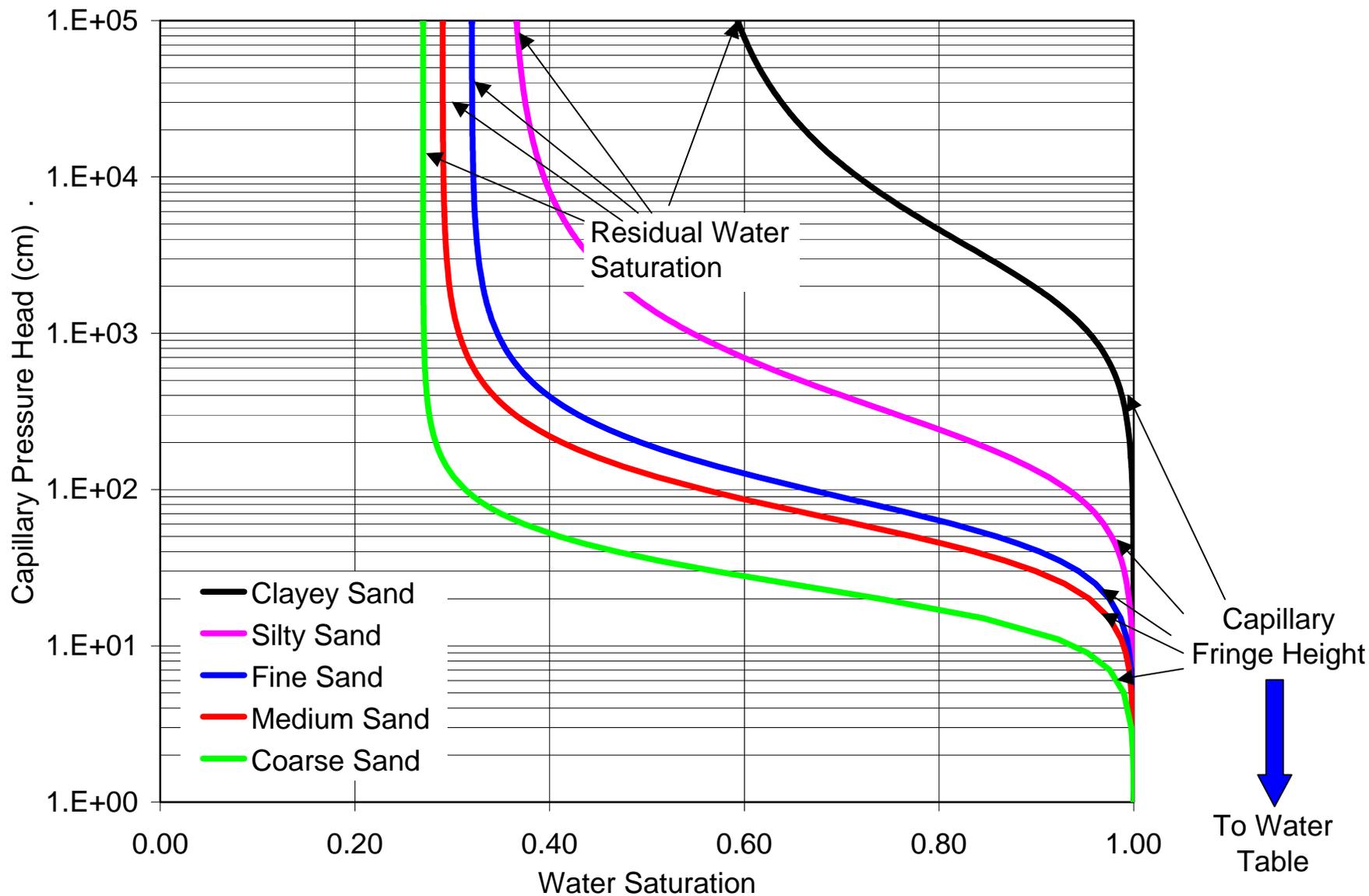
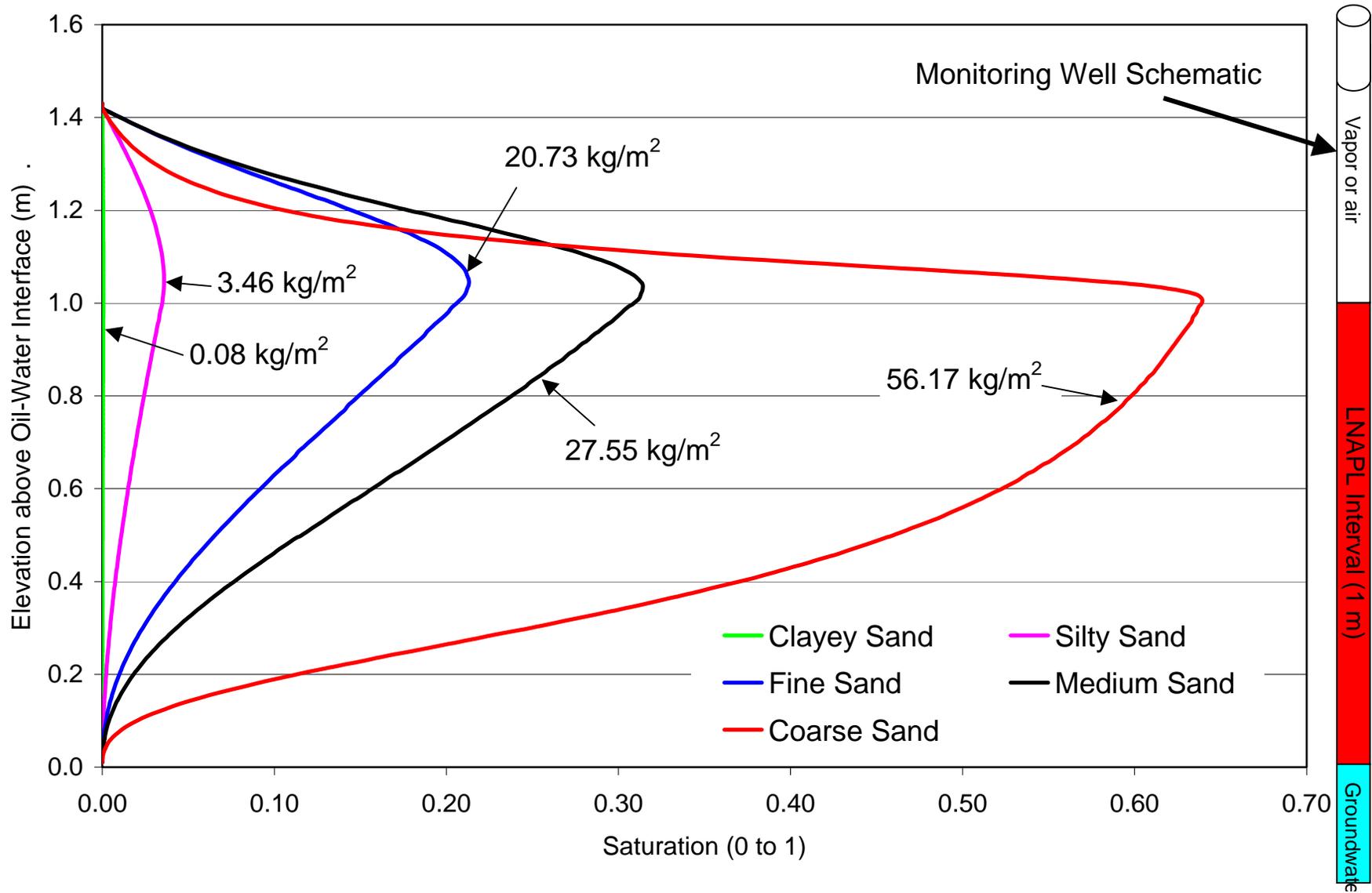
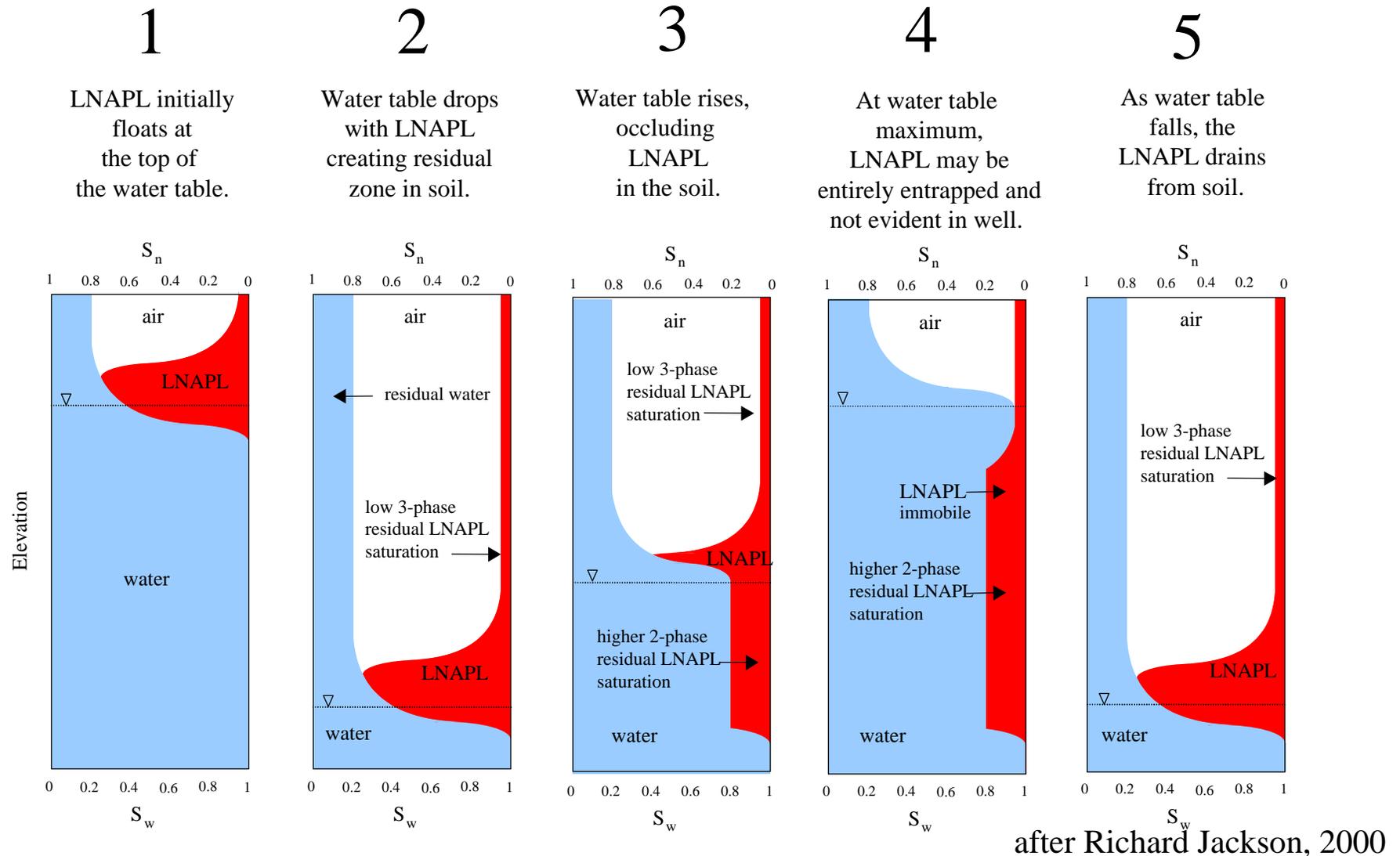


Figure 6: Theoretical LNAPL Distribution as a Function of Soil Types  
*For 1m LNAPL Thickness and Using the VEQ Model*



# Figure 7: LNAPL Thickness Under Changing Water Levels

## *Conceptual Rendering of LNAPL Occlusion*



Note:  $S_w$  = Saturation of water,  $S_n$  = Saturation of LNAPL

Figure 8: Relative Mobility of Different Products

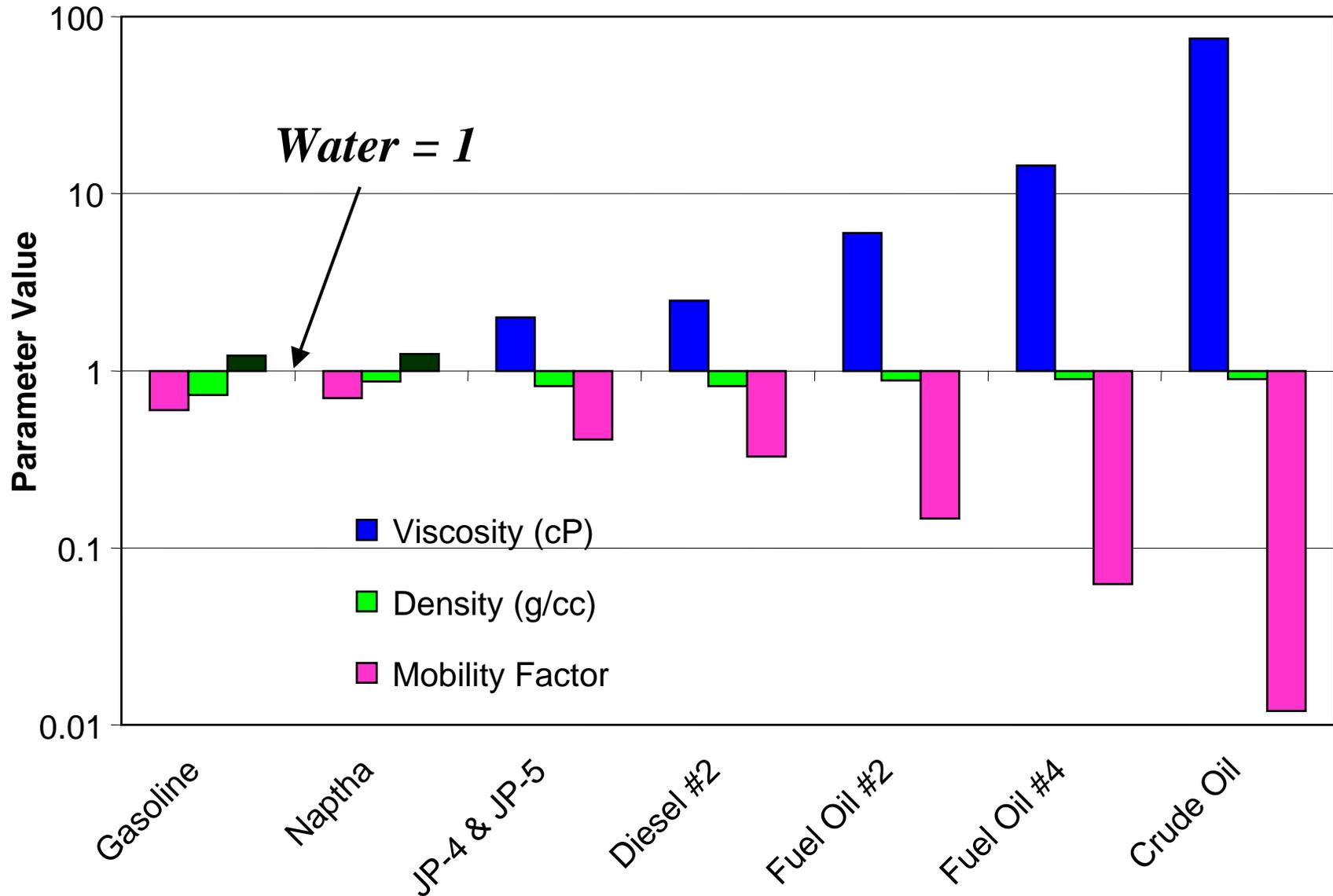


Figure 9: Dissolved Phase Arrival at Sentry Well  
(indicating plume migration, followed by free-phase LNAPL)

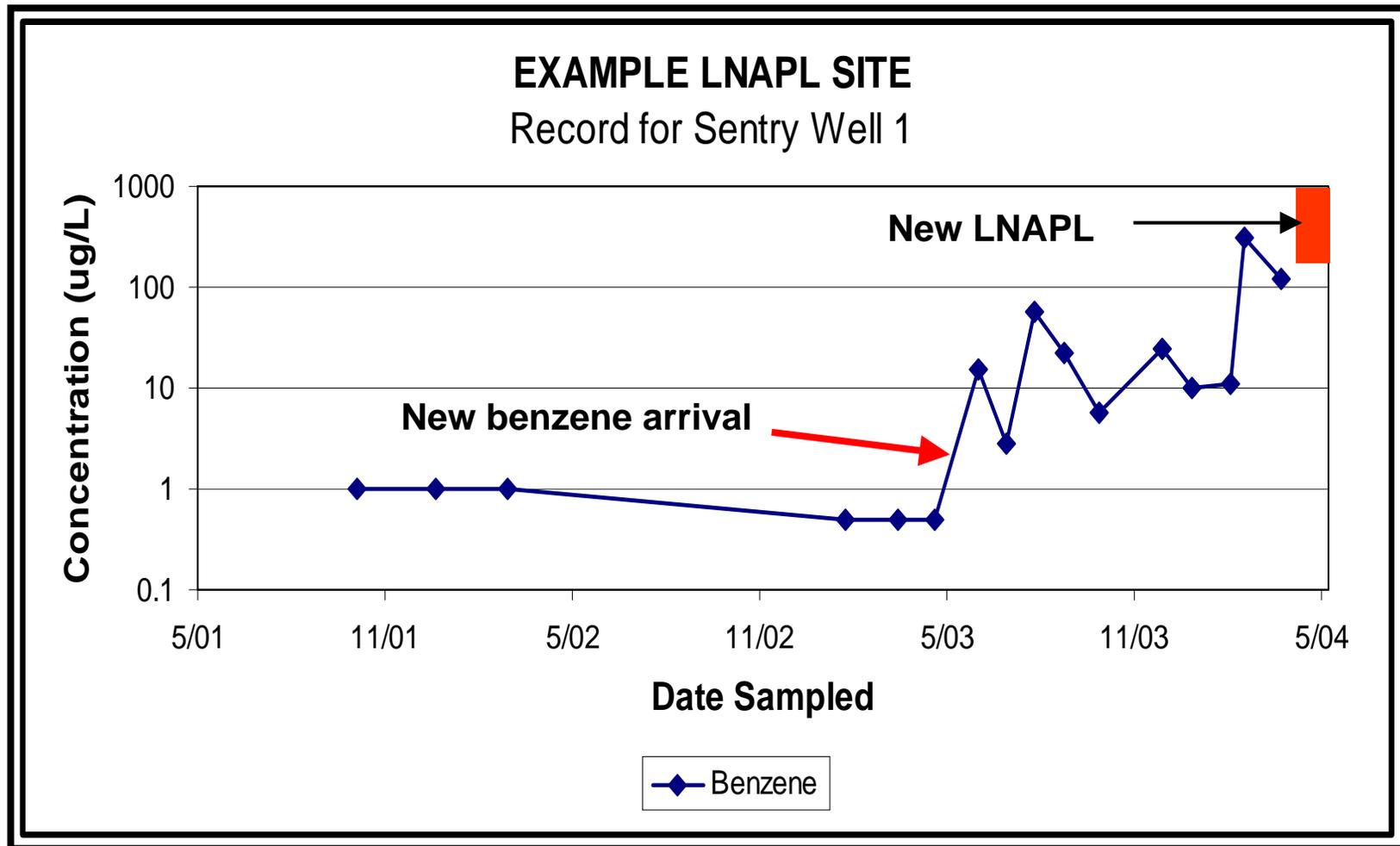


Figure 10: Downgradient Extent of CoCs  
*(as a function of soil type and 1m LNAPL thickness)*

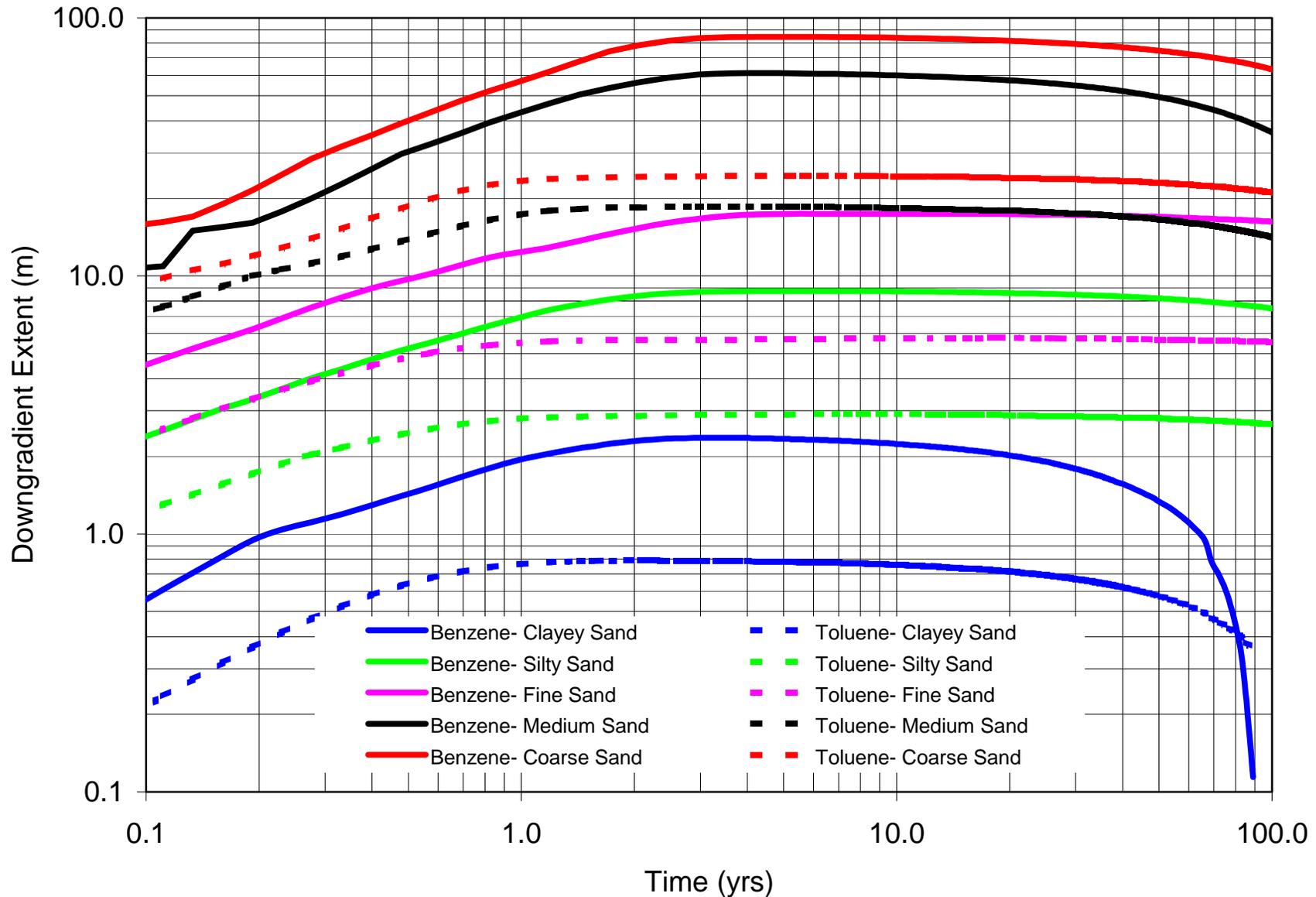


Figure 11: Partitioning of Various CoCs from Gasoline  
(*coarse soil, 1m LNAPL thickness*)

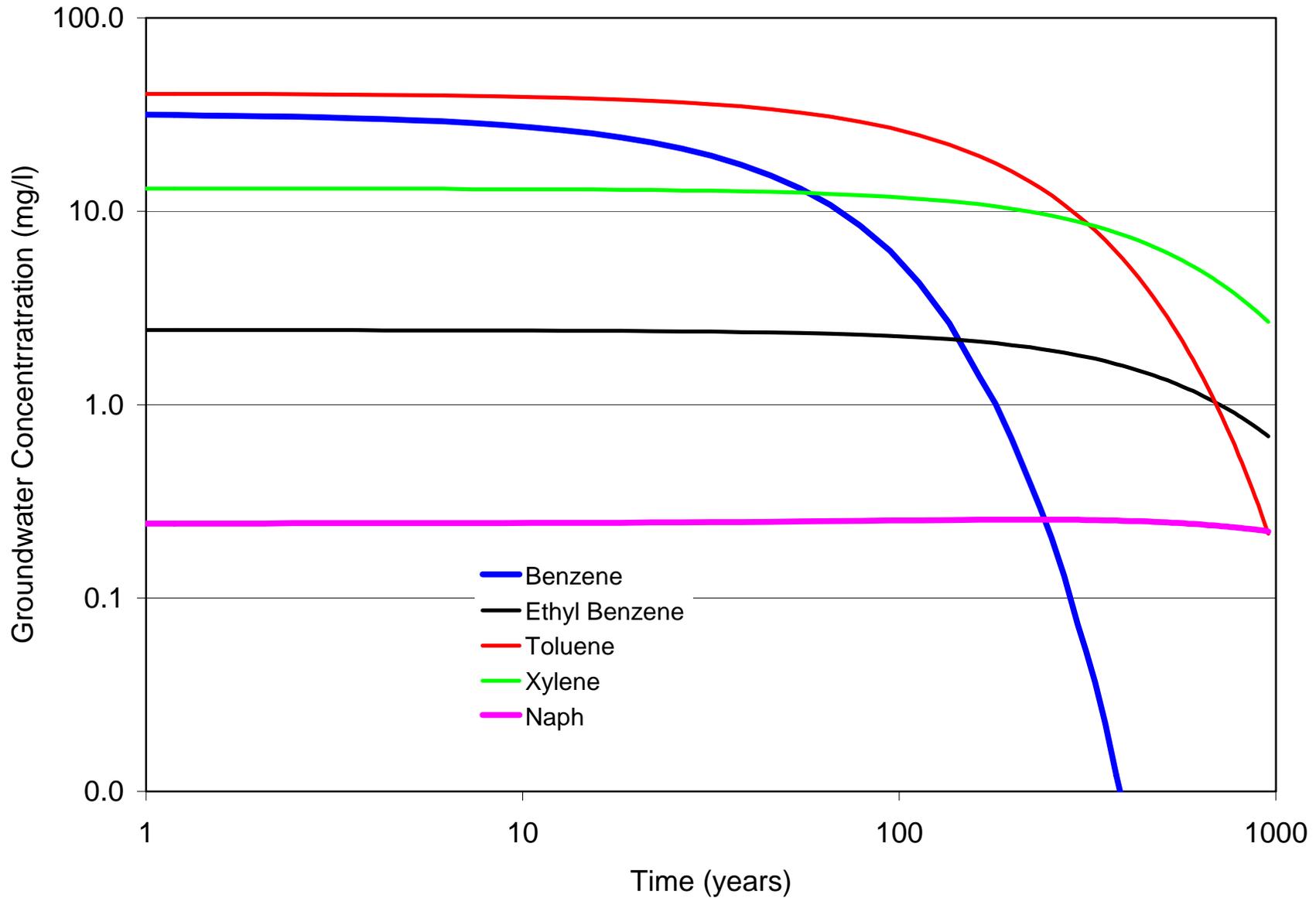


Figure 12: Gasoline vs Diesel Saturations for Two Soils  
(*VEQ Estimate, 1m LNAPL thickness*)

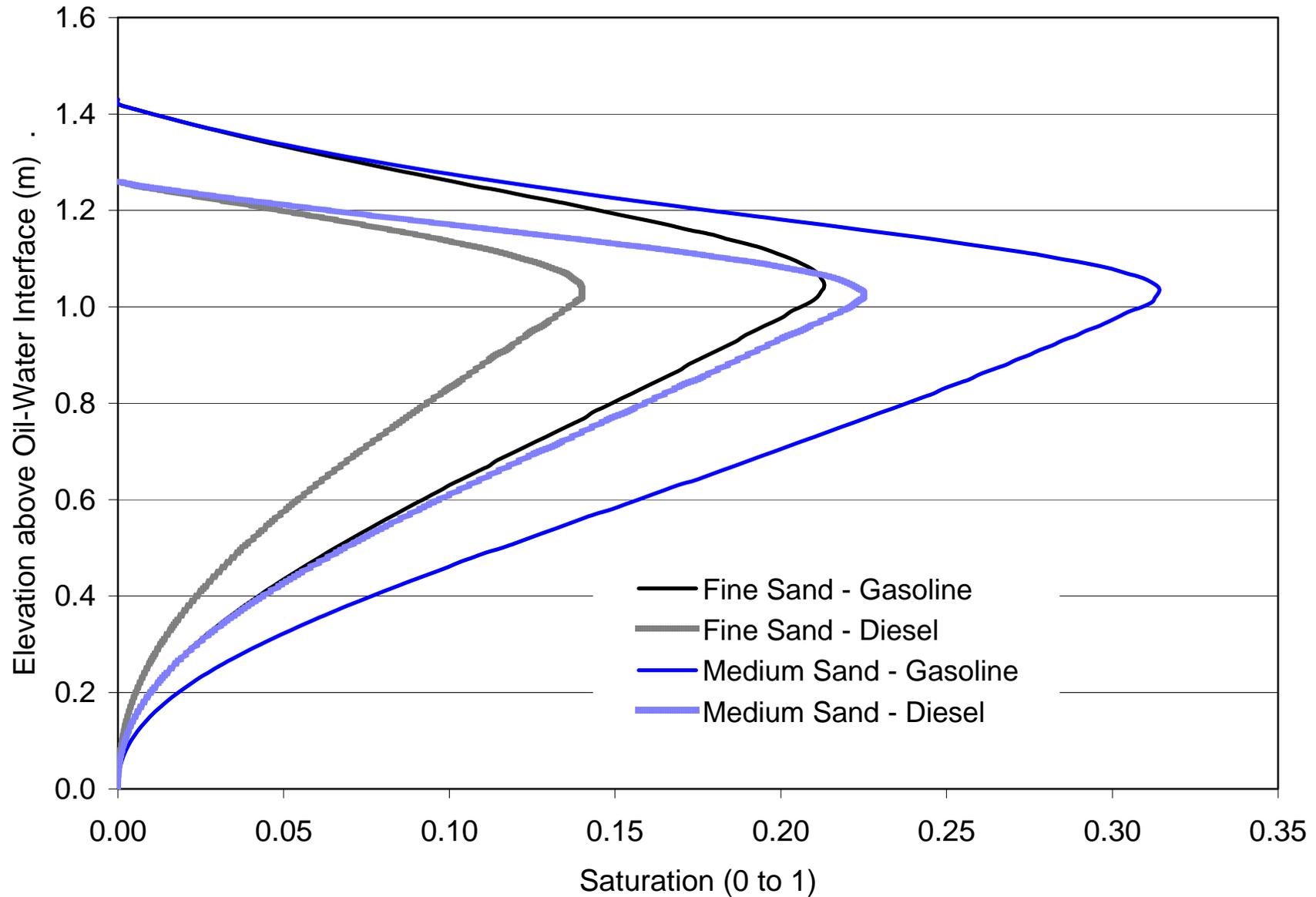


Figure 13: Heterogeneous VEQ LNAPL Distribution  
(1.5m LNAPL thickness)

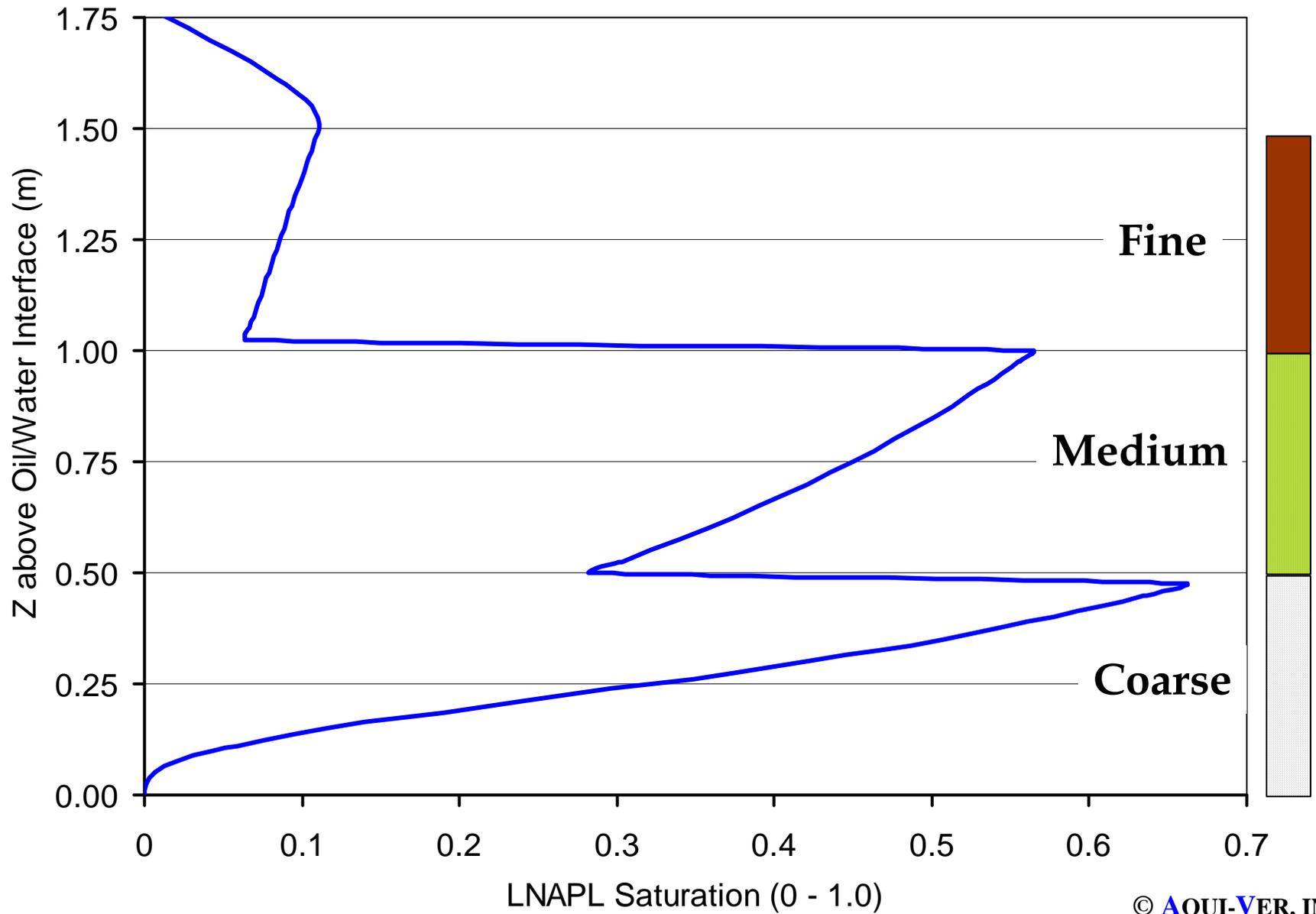


Figure 14a: Hawai'i Example of Heterogeneous VEQ Application  
*(three soil zones, VEQ model plotted against lab saturation data)*

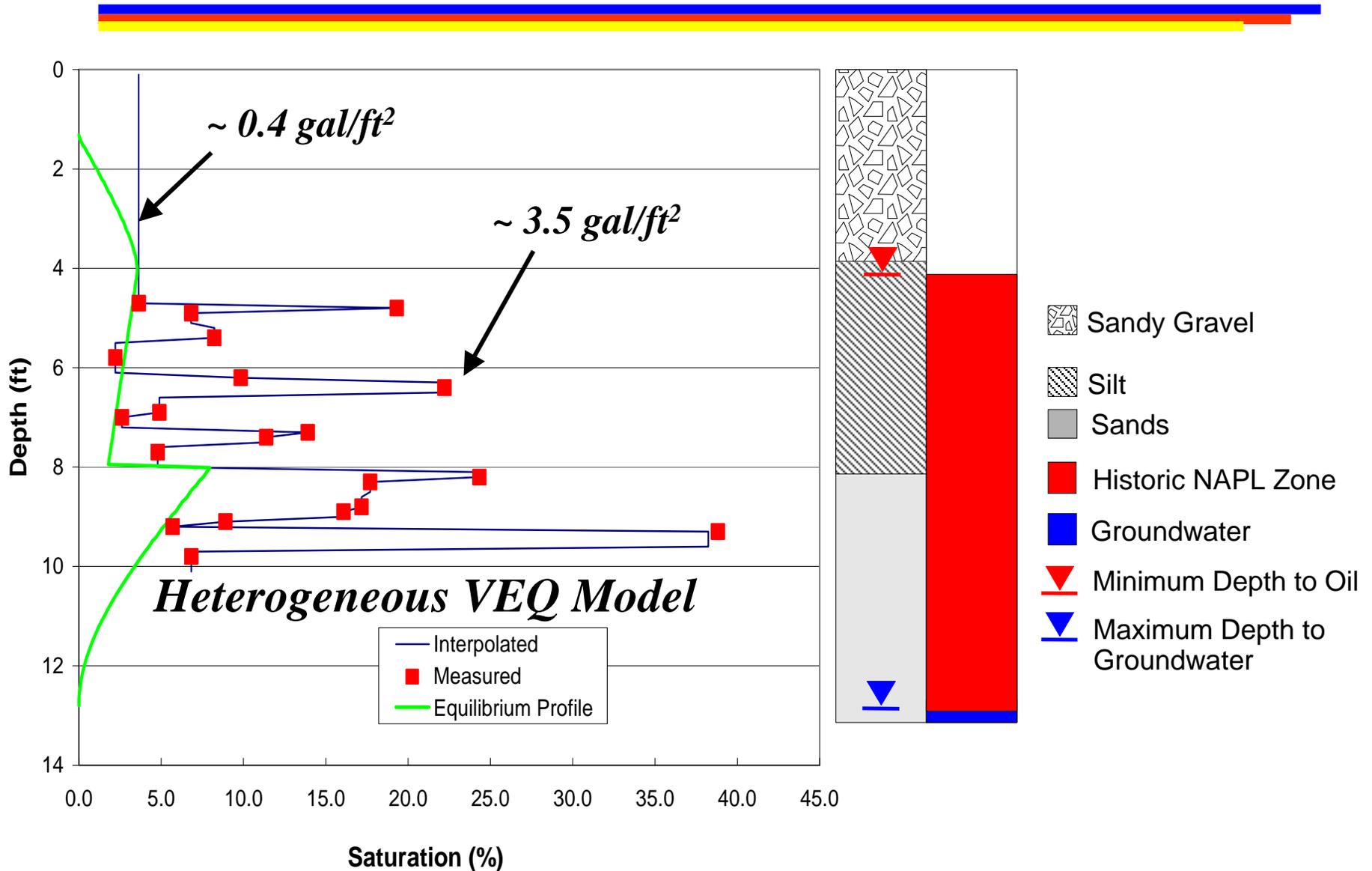
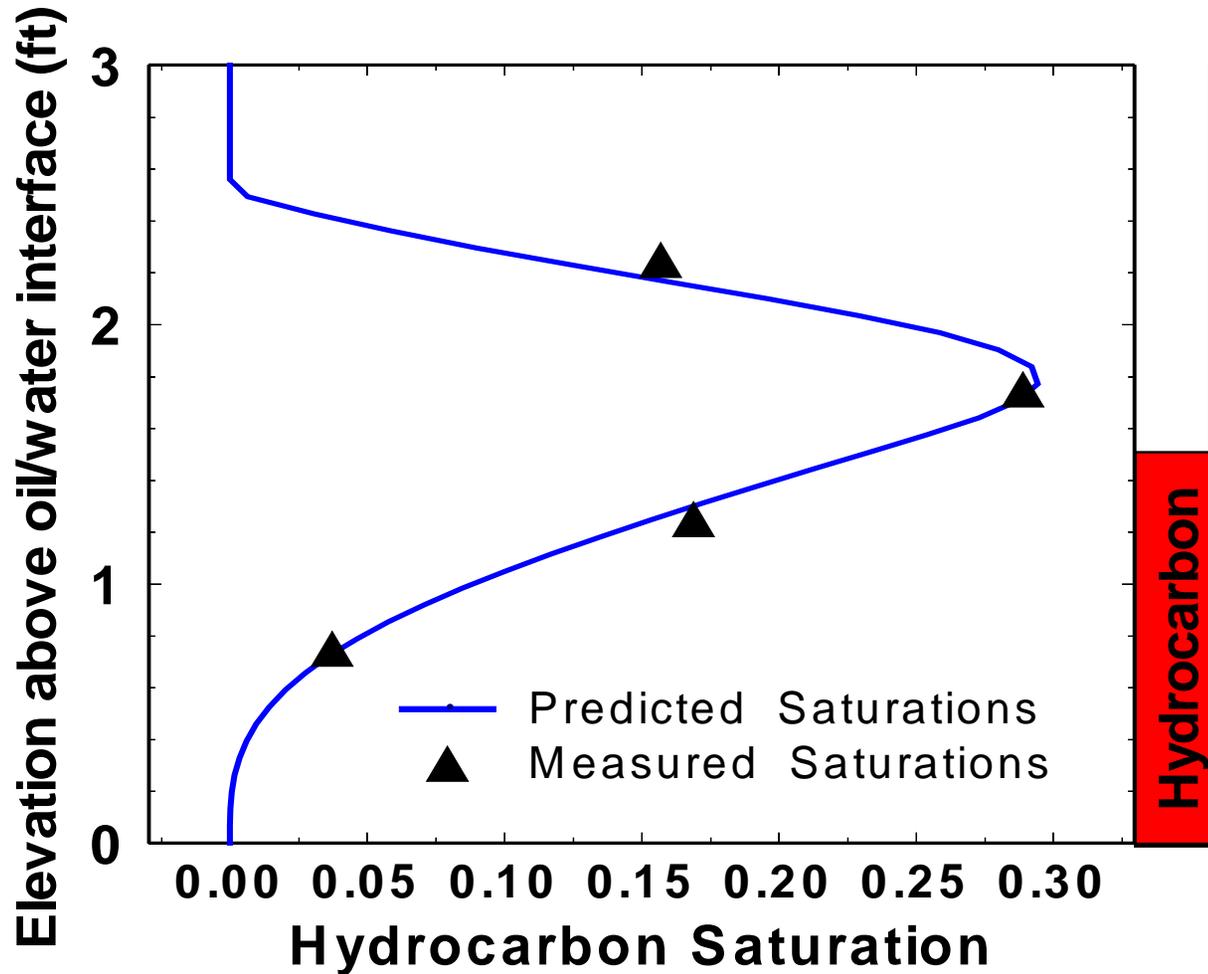
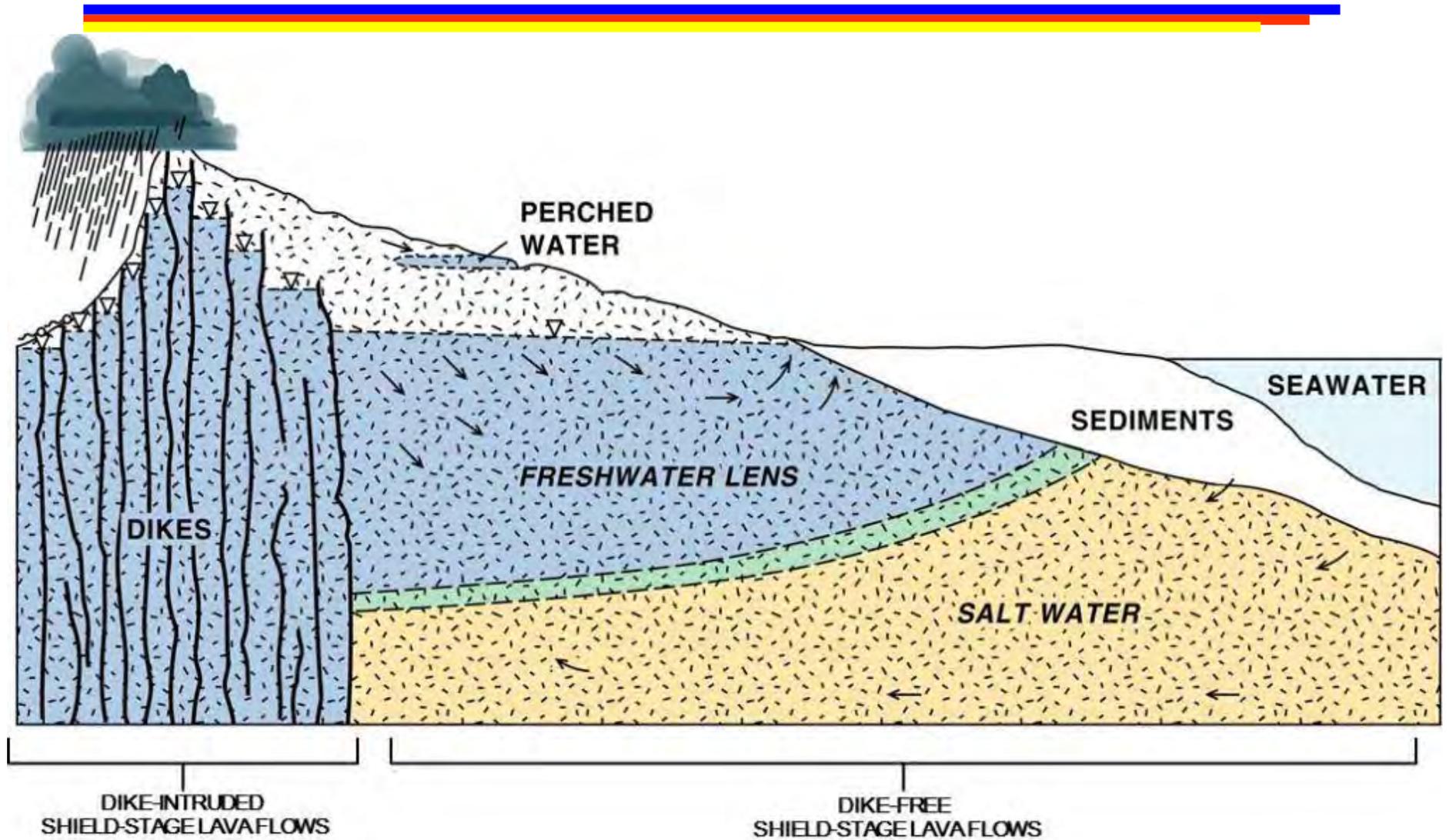


Figure 14b: VEQ Model Under Ideal Field Conditions  
(Field Measured Equilibrium LNAPL Saturation)



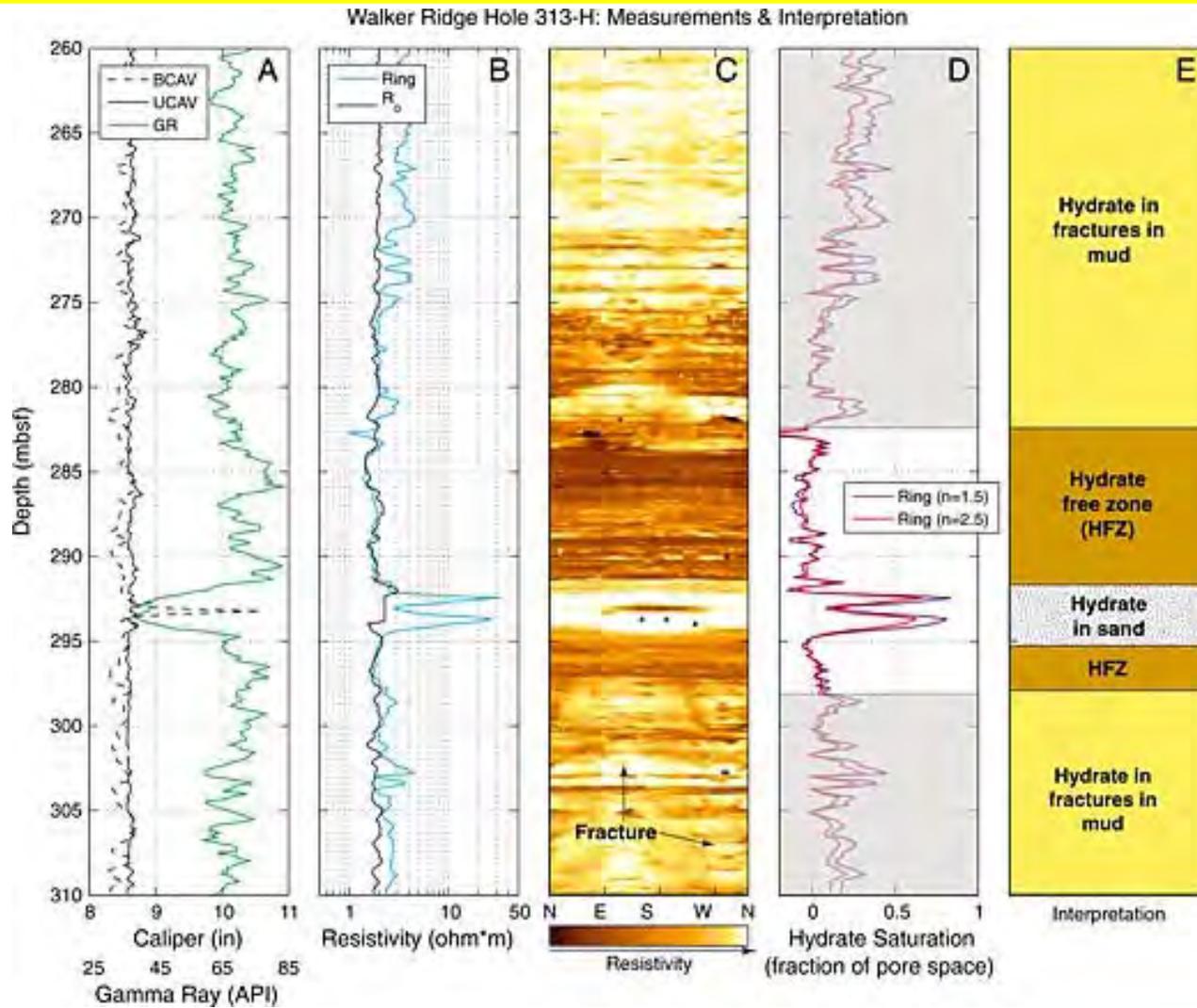
After Huntley, 1995

Figure 15: Generalized Hawai'i Hydrogeologic Setting



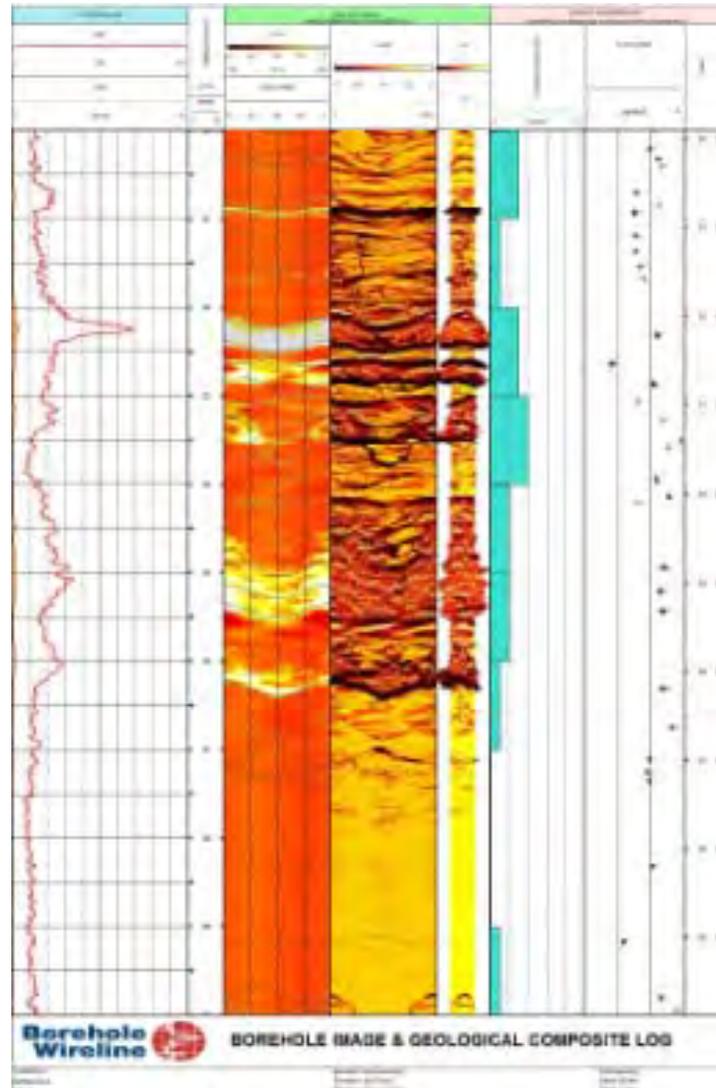
With permission; USGS Pacific Islands Water Science Center, Honolulu, Hawai'i

# Figure 16: Example Caliper and other Downhole Logs



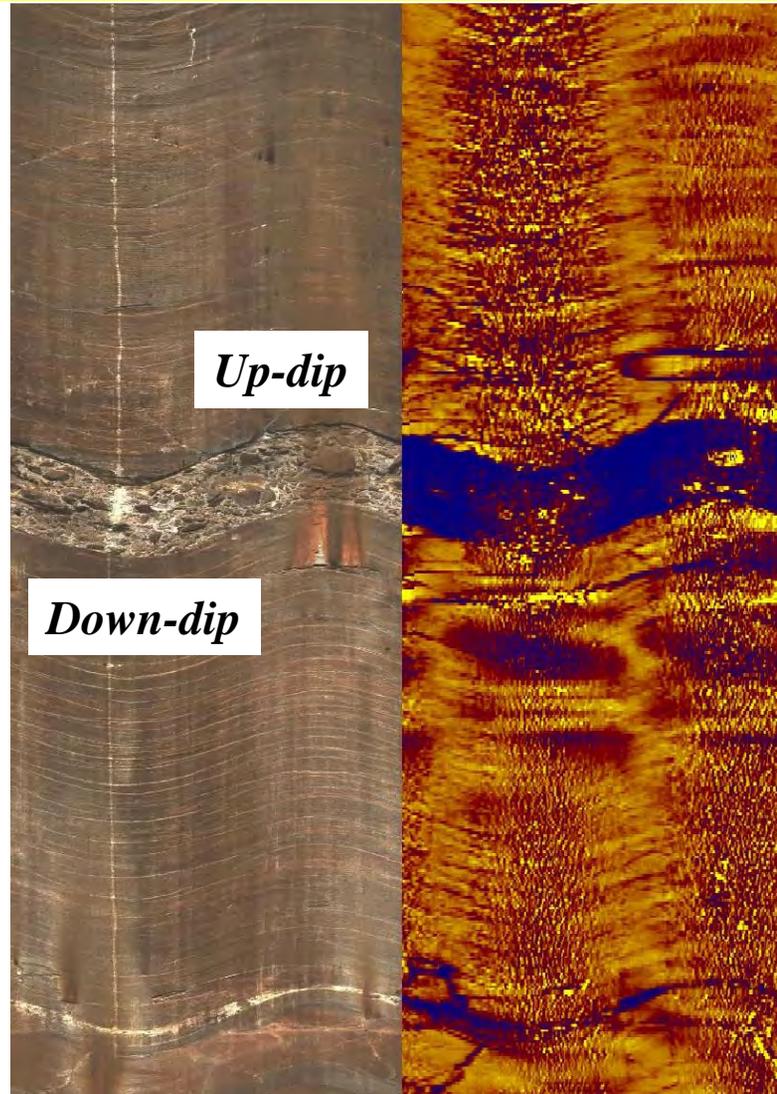
Source: Cook, A.E., Malinverno, A, 2013

# Figure 17: Processed Acoustic Televiewer Log



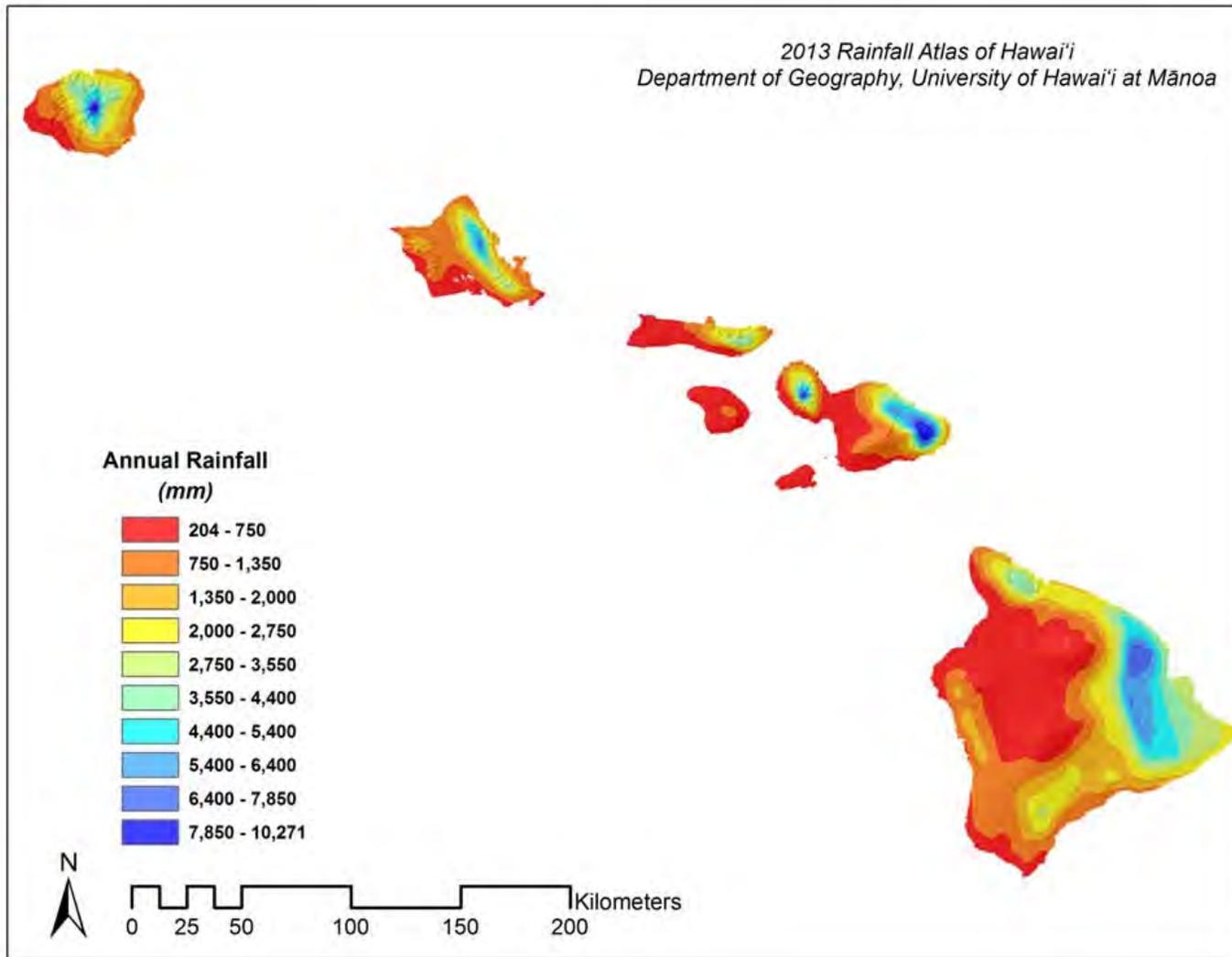
*Source: Courtesy of Borehole Wireline, Australia, 2017*

# Figure 18: Uncorrected Acoustic Televiewer Log



*Source: Courtesy of Borehole Wireline, Australia, 2017*

# Figure 19: Mean Annual Rainfall in Hawai'i



Giambelluca, T.W., Q. Chen, A.G. Frazier, J.P. Price, Y.-L. Chen, P.-S. Chu, J.K. Eischeid, and D.M. Delparte, 2013: Online Rainfall Atlas of Hawai'i. *Bull. Amer. Meteor. Soc.* 94, 313-316, doi: 10.1175/BAMS-D-11-00228.1.

**Appendix B**  
LNAPL CSM Checklists



# **Tier I Checklist**



Included ?	Item	Reference
<b>Site Name:</b>		
<b>Site Setting (Target= identification of receptors and preferential pathways, Tier categorization)</b>		
<input type="checkbox"/> Check	Are properties surrounding the site described?	
<input type="checkbox"/> Check	Is zoning described?	
<input type="checkbox"/> Check	Are current & historical site use described?	
<input type="checkbox"/> Check	Are nearby surface water described and the distance to these surface waters?	
<input type="checkbox"/> Check	Is groundwater use & classification described and distance to the closest drinking water well?	
<input type="checkbox"/> Check	Is determined if site is located above or below UIC line ?	
<input type="checkbox"/> Check	Are current & historical site features mentioned and shown?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are any buildings used on site or is known where buildings will be placed in the future?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are contents, capacities of past and present storage containers described?	Map Current And Historical Site Features-Table - container/AST/UST number with contents and capacities by year
<input type="checkbox"/> Check	Are there utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways	Map-Utility Corridors & Preferential Pathways
<input type="checkbox"/> Check	Is described what the onsite surface cover is (soil, asphalt, concrete, liners) ?	Map -Current And Historical Site Features/Surface Cover
<input type="checkbox"/> Check	Have field observations been recorded (odor, staining, free product/sheen observations, PID readings)?	Table PID screening values/Boring Logs; Map of Product Observations
<input type="checkbox"/> Check	Has geology and permeability been described	Profiles -along site and across site
<input type="checkbox"/> Check	Is described if any areas were excavated or where remediation features are located and what the radius of influence is (as determined by pilot tests preferentially or from specs if necessary)	Map- Remediation Features/Remedial Excavation Features
<b>LNAPL Characteristics</b>		
<input type="checkbox"/> Check	Is the type of product released described, the year when released , and the release volume?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Is determined if product released has high or low viscosity?	
<input type="checkbox"/> Check	Has been identified if there has been one or multiple releases/LNAPL plumes?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Have different types of product been identified in the field indicating different/multiple releases?	Map of different type of LNAPL encountered in soil and groundwater (e.g. based on field observations-color, viscosity)
<input type="checkbox"/> Check	Have LNAPL, soil, groundwater, and/or vapor data been evaluated regarding source material?	Maps of COC and COPC that indicate different sources or source location
<input type="checkbox"/> Check	Have potentially very mobile (polar) COCs be identified (e.g., MTBE, fuel oxygenates)?	Maps of mobile COPCs on groundwater
<input type="checkbox"/> Check	Have potentially very volatile COCs be identified?	Maps of volatile COPCs in vapor
<b>Characterization of LNAPL in Dynamic Environment</b>		
<b>(Providing Context And Understanding What Drives LNAPL/Contaminant Distribution)</b>		
<input type="checkbox"/> Check	Has extent of LNAPL contamination in soil below the water table been explored (trapped LNAPL)?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Have data "outliers" been investigated and explained? (e.g., is there another evidence indicating a release, is there indication of rapid dewatering during sampling or was the water level unusually high so that a shallow source may have been tapped)?	

Checklist for Simple Sites (Tier I)

Check Has the groundwater gradient been determined at high and low tide and been corrected for the presence of free product? Maps of groundwater gradients

**LNAPL plume delineation and Determination of Source Zones**

Check Has the extent of free product (Free product footprint) been determined at maximum free product level (e.g., for unconfined situations lowest water level, confined at highest water level) LNAPL Footprint Maps

Check Has the extent of residual LNAPL been determined laterally and vertically and displayed together with LNAPL occurrences in soil & gw? Determination of LNAPL in 3-D from combined data of lowest & highest water level, staining and other field observations) LNAPL Footprint and residual LNAPL Maps & Profiles, PID tables, field observations (Appendix)

Check Has potential offsite and onsite migration been discussed?

Check Has been determined if LNAPL is mobile? If it is mobile- is it also migrating? LNAPL Footprint maps compared through time at same water level.

Check Have all available data been combined to show LNAPL distribution (free and residual product) and been easily displayed on a map (free product, odor & staining observation, glove tests, paper towel tests, TPH concentrations and calculated saturation percentages, sheen observations, different types of products identified by color or viscosity) Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL

Check Has extent of LNAPL in soil (free product plus residual LNAPL) been extrapolated to shallow depth at source container? Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL

Check Has deepest extent of LNAPL occurrence been determined below water table and LNAPL extent been extrapolated to at least lowest stand of water level in saturated zone? Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL

Check Has the largest extent of the groundwater plume been determined based on high mobility contaminants (e.g., ethanol, MTBE, benzene)? Contour Maps- COC in groundwater & COCs in vapor

Check Have source areas been identified for secondary groundwater and vapor plumes? (e.g., by mapping low(er)-mobility COCs in groundwater such as TPH-g/d/o, naphthalene, X, E, 1-Methylnaphthalene, 2-Methylnaphthalene) Maps- COC in groundwater & COCs in vapor

Check Have groundwater field data (physical water quality data) been determined and calibrated to determine redox situation and been displayed on a map? (e.g. dissolved oxygen, pH, conductivity, or redox potential)? Low DO, high conductivity, and change in pH may indicate source zones. Redox zone or physical parameters map.

Check Have MNA groundwater data be obtained (methane, Mn<sup>2+</sup>, Fe<sup>2+</sup>, sulfate, sulfide, nitrate, carbonate) to determine biodegradation presence, redox, and source zones? More reducing (e.g., methanogenic) areas indicate proximity to source areas and potential vapor intrusion hazard areas. Redox zone or physical parameters map.

Check Is there any other evidence for the presence of methanogenic zones (e.g. low MTBE/TBA) ratios? Groundwater Concentrations (or concentration ratios) map

Check Have TPH-Chromatograms been submitted that could indicate interferences and provide information about degradation? (e.g., production of low C range aliphatics under methanogenic conditions)? Appendix Chromatograms

Check Have groundwater concentration maps been submitted that include concentrations at effective saturation levels for those wells that contained free product and were not sampled for groundwater? Groundwater Concentration contour maps or graphs

## Checklist for Simple Sites (Tier I)

- Check Have vapor data been collected that could indicate the location of the main LNAPL mass (source) and been displayed on a map? Vapor concentration contour maps

### LNAPL Mobility/Plume Stage

- Check Have high permeability lithologies or zones been identified (e.g. fractured rock, gravel, coralline lithologies, lava tubes etc.)?
- Check Has LNAPL thickness and presence/absence in wells been shown at similar water table levels for different years? LNAPL Footprint Maps
- Check Have LNAPL gradients and water table gradients been determined for the same data set for different years? LNAPL Gradient Maps
- Check Have areas been identified where LNAPL is locally mobile (e.g., during tidal/seasonal changes) versus laterally mobile (migrating)? LNAPL Footprint Maps
- Check If lab petrophysical tests have been conducted- were samples collected from enough boring locations and situations to be representative of the whole site? Petrophysical results maps, tables, Appendix
- Check Have pore saturations been determined using TPH concentrations? Petrophysical results maps, tables
- Check Has the plume stage been defined? How?
- Check Has been proven that the release is not ongoing? Groundwater concentration (and concentration ratios maps)
- Check Has movement along potential preferential pathways been shown to not occur (e.g. no intersection of LNAPL footprint with preferential pathways, no product observations in preferential pathways or outfalls). Preferential pathways (utility) Map and LNAPL footprint map, Photographs
- Check Do dissolved concentrations decrease as shown in graph if COC versus time? Graphs-groundwater concentration (or concentration ratios) versus time
- Check If statistical analysis was applied (aka Mann-Kendall) to show stable/decreasing/increasing conc., were data points excluded as "outliers"? If so, it needs to be explained why and what likely caused the deviation, so that a potential release causing high conc. won't be ignored. Note that if seasonal variations are identified, the seasonal Mann-Kendall test should be applied.
- Check If Mann-Kendall analysis was applied, are the graphs shown on a concentration-time diagram together with the data? Graphs-groundwater concentration (or concentration ratios) versus time
- Check Have geological cross sections with depth of contamination been prepared along site and across site? Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall

### Risk

- Check Has Short term vapor emission (including methane) from LNAPL, sheens, water, and ignition of vapor been investigated? groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
- Check Has long-term vapor emission/intrusion into overlying or nearby buildings, and vapor migration into onsite or offsite utility corridors or preferential pathways been investigated? groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
- Check Has migration of LNAPL into surface waters, storm drains, or other preferential pathways been investigated? LNAPL footprint & groundwater COPC maps, preferential pathway maps
- Check Has groundwater contamination and potential offsite migration onto nearby properties or surface water habitats been investigated? LNAPL footprint & groundwater COPC maps, preferential pathway maps
- Check Has protection of onsite or offsite workers or populations during construction been addressed? groundwater volatile COC maps, vapor maps, preferential pathway maps

## Checklist for Simple Sites (Tier I)

- Check Is there an increased risk in methane accumulation due to onsite liners and potentially lateral migration of vapors & methane groundwater and vapor methane maps or graphs through time

### Remediation Considerations

- Check Were source zones targeted for remediation Map of remediation features, LNAPL footprint maps;
- Check Were high permeability zones targeted for LNAPL extraction Profiles along site and across site
- Check Was the ROI as determined through pilot test sufficient to affect and extract the free LNAPL. Map of remediation features, LNAPL footprint maps;
- Check Did remediation system target the correct depth (E.g. vadose zone or saturated zone) Profiles along site and across site. LNAPL footprint Maps
- Check Has been demonstrated that MNA and NSZD is occurring. MNA parameter maps & graphs
- Check Have remediation timeframes been established for all proposed remedial options (default "reasonable timeframe" is 30 years) Table remediation timeframes
- Check Have remedial endpoints been established for each evaluated remediation option Table remediation endpoints
- Check If a remediation system was turned off- was investigated if rebound conditions occurred? LNAPL footprint maps or graphs of LNAPL thickness variation through time for the same DTW; Graphs of concentration variations through time

### Maps/Profiles

- Check Site Location
- Check Current And Historical Site Features with the following:
- Check Box 1 Pipeline, USTs, ASTs, Oil/Water Separators, Tanker Truck Loading Racks, Tank Farm Walls (include content by year & capacity)
- Check Box 1 Utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways
- Check Box 1 Areas of current/historical pavement (asphalt, concrete) and or other surface covers such as liners?
- Check Box 1 Areas excavated, remediated, locations of remediation features and radius of influence of remediation features (as determined by pilot tests preferentially or from specs if necessary)
- Check Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall
- Check Product Occurrence -Different types based on observations of color, viscosities etc.
- Check COCs above EALs in soil, groundwater and soil vapor maps (soil by DU; gw and sv contour maps)
- Check COPCs (or COPC ratios) that are indicators of different sources (e.g. MTBE, Ethanol, lead)- soil, sv, gw (contour maps)
- Check COPCs in groundwater or vapor (contour maps) that are indicators of residual sources (e.g.,less mobile COPC such as napthalene, xylene) or COPCs/parameters indicating residual sources (e.g. methane or other anaerobic degradation products; low pH conditions, low oxygen zones, areas of high conductivity, thermal anomalies; low MTBE/TBA zones, high TPH-d SGC/TPH-d areas)
- Check LNAPL footprint maps at maximum LNAPL thickness (lowest water level for unconfined, highest water level for confined conditions) through time
- Check Free LNAPL and residual LNAPL map in 3 D (Maps & profiles)
- Check Redox zones (contours) based on groundwater MNA parameters (Methane, sulfate/sulfide/nitrate/Fe2+, Mn2+) and/or physical parameters (e.g., pH, redox potential, heat, conductivity)
- Check Methane Vapor Data

## Checklist for Simple Sites (Tier I)

Check LNAPL Gradient Maps

### Tables

- Check Tank (UST/AST) contents and capacities
- Check PID Screening values
- Check Release Sources, Years, and Volumes
- Check LNAPL Thickness Data with Date, DTW and DTP
- Check Soil Data
- Check Vapor Data (including methane, H<sub>2</sub>S, CO<sub>2</sub>, and O<sub>2</sub> Data)
- Check Groundwater Data with Date, Time, and DTW
- Check

### Graphs

- Check Groundwater concentration graphs versus time with water table versus time and/or rainfall data versus time
- Check LNAPL thickness variations vs time at same DTW

### Appendices

- Check Laboratory Reports
- Check TPH chromatograms (TPH-g, TPH-d, and TPH-o) for soil, groundwater, vapor and LNAPL
- Check Boring Logs & Well Installation Logs with soil description, odor & staining description
- Check Photo Logs



# **Tier II Checklist**



Included ?	Item	Reference
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Site Name:

**Site Setting (Target= identification of receptors and preferential pathways, Tier categorization)**

<input type="checkbox"/> Check	Are properties surrounding the site described?	
<input type="checkbox"/> Check	Is zoning described?	
<input type="checkbox"/> Check	Are current & historical site use described?	
<input type="checkbox"/> Check	Are nearby surface water described and the distance to these surface waters?	
<input type="checkbox"/> Check	Is groundwater use & classification described and distance to the closest drinking water well?	
<input type="checkbox"/> Check	Is determined if site is located above or below UIC line ?	
<input type="checkbox"/> Check	Are current & historical site features mentioned and shown?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are any buildings used on site or is known where buildings will be placed in the future?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are contents, capacities of past and present storage containers described?	Map Current And Historical Site Features-Table - container/AST/UST number with contents and capacities by year
<input type="checkbox"/> Check	If Tank Farm Walls are present- Is described how far they reach into groundwater?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are there utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways	Map-Utility Corridors & Preferential Pathways
<input type="checkbox"/> Check	Is described what the onsite surface cover is (soil, asphalt, concrete, liners) ?	Map -Current And Historical Site Features/Surface Cover
<input type="checkbox"/> Check	Have field observations been recorded (odor, staining, free product/sheen observations, PID readings)?	Table PID screening values/Boring Logs; Map of Product Observations
<input type="checkbox"/> Check	Has geology and permeability been described	Profiles -along site and across site
<input type="checkbox"/> Check	Is described if any areas were excavated or where remediation features are located and what the radius of influence is (as determined by pilot tests preferentially or from specs if necessary)	Map- Remediation Features/Remedial Excavation Features

**LNAPL Characteristics**

<input type="checkbox"/> Check	Is the type of product released described, the year when released , and the release volume?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Is determined if product released has high or low viscosity?	
<input type="checkbox"/> Check	Has been identified if there has been one or multiple releases/LNAPL plumes?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Have different types of product been identified in the field indicating different/multiple releases?	Map of different type of LNAPL encountered in soil and groundwater (e.g. based on field observations-color, viscosity)
<input type="checkbox"/> Check	Have LNAPL, soil, groundwater, and/or vapor data been evaluated regarding source material?	Maps of COC and COPC that indicate different sources or source location
<input type="checkbox"/> Check	Have potentially very mobile (polar) COCs be identified (e.g., MTBE, fuel oxygenates)?	Maps of mobile COPCs on groundwater
<input type="checkbox"/> Check	Have potentially very volatile COCs be identified?	Maps of volatile COPCs in vapor
<input type="checkbox"/> Check	Has type or "aged" character of LNAPL been defined in any other way if release time is unknown? (e.g., lead in gasoline, MTBE or other oxygenates, sulfur content, different additives, viscosity, fingerprint analysis)	Maps of "age"-defining COPCs

Included ?	Item	Reference
<b>Characterization of LNAPL in Dynamic Environment</b>		
<b>(Providing Context And Understanding What Drives LNAPL/Contaminant Distribution)</b>		
<input type="checkbox"/> Check	Has the relationship between LNAPL and water table change (tidal/seasonal) and COC concentration in groundwater and water table been investigated (e.g., tapping of shallow sources)? Has at key locations been determined if groundwater is under confined or unconfined conditions?	Graphs of LNAPL thickness and COC concentrations in groundwater vs. water table
<input type="checkbox"/> Check	Has extent of LNAPL contamination in soil below the water table been explored (trapped LNAPL)?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of tank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Have LNAPL readings been systematic collected at the same stage of the tide, accounting for lag of time of tidal influence distant from the coast?	
<input type="checkbox"/> Check	Have data "outliers" been investigated and explained? (e.g., is there another evidence indicating a release, is there indication of rapid dewatering during sampling or was the water level unusually high so that a shallow source may have been tapped)?	
<input type="checkbox"/> Check	Do plots of concentrations ratios in groundwater with the same denominator indicate mixing of different groundwater plumes (different releases)?	Graphs of concentration ratios with same denominator
<input type="checkbox"/> Check	Has the groundwater gradient been determined at high and low tide and been corrected for the presence of free product?	Maps of groundwater gradients
<input type="checkbox"/> Check		
<b>LNAPL plume delineation and Determination of Source Zones</b>		
<input type="checkbox"/> Check	Has the extent of free product (Free product footprint) been determined at maximum free product level (e.g., for unconfined situations lowest water level, confined at highest water level)	LNAPL Footprint Maps
<input type="checkbox"/> Check	Has the extent of residual LNAPL been determined laterally and vertically and displayed together with LNAPL occurrences in soil & gw? Determination of LNAPL in 3-D from combined data of lowest & highest water level, staining and other field observations)	LNAPL Footprint and residual LNAPL Maps & Profiles, PID tables, field observations (Appendix)
<input type="checkbox"/> Check	Has potential offsite and onsite migration been discussed?	
<input type="checkbox"/> Check	Has the mass of LNAPL (free and residual) been estimated (e.g. by using concentrations per volume/unit area)?	
<input type="checkbox"/> Check	Has been determined if LNAPL is mobile? If it is mobile- is it also migrating?	LNAPL Footprint maps compared through time at same water level.
<input type="checkbox"/> Check	Have all available data been combined to show LNAPL distribution (free and residual product) and been easily displayed on a map (free product, odor & staining observation, glove tests, paper towel tests, TPH concentrations and calculated saturation percentages, sheen observations, different types of products identified by color or viscosity)	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has extent of LNAPL in soil (free product plus residual LNAPL) been extrapolated to shallow depth at source container?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has deepest extent of LNAPL occurrence been determined below water table and LNAPL extent been extrapolated to at least lowest stand of water level in saturated zone?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL

Checklist for More Complex Sites (Tier II)

Included ?	Item	Reference
<input type="checkbox"/> Check	Has the largest extent of the groundwater plume been determined based on high mobility contaminants (e.g., ethanol, MTBE, benzene)?	Contour Maps- COC in groundwater & COCs in vapor
<input type="checkbox"/> Check	Have source areas been identified for secondary groundwater and vapor plumes? (e.g., by mapping low(er)-mobility COCs in groundwater such as TPH-g/d/o, naphthalene, X, E, 1-Methylnaphthalene, 2-Methylnaphthalene)	Maps- COC in groundwater & COCs in vapor
<input type="checkbox"/> Check	Have groundwater field data (physical water quality data) been determined and calibrated to determine redox situation and been displayed on a map? (e.g. dissolved oxygen, pH, conductivity, or redox potential)? Low DO, high conductivity, and change in pH may indicate source zones.	Redox zone or physical parameters map.
<input type="checkbox"/> Check	Have MNA groundwater data be obtained (methane, Mn <sup>2+</sup> , Fe <sup>2+</sup> , sulfate, sulfide, nitrate, carbonate) to determine biodegradation presence, redox, and source zones? More reducing (e.g., methanogenic) areas indicate proximity to source areas and potential vapor intrusion hazard areas.	Redox zone or physical parameters map.
<input type="checkbox"/> Check	Is there any other evidence for the presence of methanogenic zones (e.g. low MTBE/TBA) ratios?	Groundwater Concentrations (or concentration ratios) map
<input type="checkbox"/> Check	Have TPH-Chromatograms been submitted that could indicate interferences and provide information about degradation? (e.g., production of low C range aliphatics under methanogenic conditions)?	Appendix Chromatograms
<input type="checkbox"/> Check	Has the extent and behavior of mobile versus less/non-mobile compounds in groundwater been evaluated (e.g., B/X or B/naphthalene ratios B/TPH-g ratios with time and level of water)?- less mobile COCs are typically closer to the source and relatively more enriched with time; enhanced mobility at high water levels could indicate dissolution of shallow source or a new release- this should be distinguished	Groundwater Concentrations (or concentration ratios) contour map or graphs
<input type="checkbox"/> Check	Have groundwater concentration maps been submitted that include concentrations at effective saturation levels for those wells that contained free product and were not sampled for groundwater?	Groundwater Concentration contour maps or graphs
<input type="checkbox"/> Check	Have vapor data been collected that could indicate the location of the main LNAPL mass (source) and been displayed on a map?	Vapor concentration contour maps

**LNAPL Mobility/Plume Stage**

<input type="checkbox"/> Check	Have high permeability lithologies or zones been identified (e.g. fractured rock, gravel, coralline lithologies, lava tubes etc.)?	
<input type="checkbox"/> Check	Has LNAPL thickness and presence/absence in wells been shown at similar water table levels for different years?	LNAPL Footprint Maps
<input type="checkbox"/> Check	Have LNAPL gradients and water table gradients been determined for the same data set for different years?	LNAPL Gradient Maps
<input type="checkbox"/> Check	Have areas been identified where LNAPL is locally mobile (e.g., during tidal/seasonal changes) versus laterally mobile (migrating)?	LNAPL Footprint Maps
<input type="checkbox"/> Check	If fluid saturations have been determined from TPH concentrations were enough and representative samples collected (e.g., MI samples)?	
<input type="checkbox"/> Check	Has the plume stage been defined?	How?
<input type="checkbox"/> Check	Has been proven that the release is not ongoing?	Groundwater concentration (and concentration ratios maps)

Checklist for More Complex Sites (Tier II)

Included ?	Item	Reference
<input type="checkbox"/> Check	Has movement along potential preferential pathways been shown to not occur (e.g. no intersection of LNAPL footprint with preferential pathways, no product observations in preferential pathways or outfalls).	Preferential pathways (utility) Map and LNAPL footprint map, Photographs
<input type="checkbox"/> Check	Do dissolved concentrations decrease as shown in graph if COC versus time?	Graphs-groundwater concentration (or concentration ratios) versus time
<input type="checkbox"/> Check	If statistical analysis was applied (aka Mann-Kendall) to show stable/decreasing/increasing conc., were data points excluded as "outliers"? If so, it needs to be explained why and what likely caused the deviation, so that a potential release causing high conc. won't be ignored. Note that if seasonal variations are identified, the seasonal Mann-Kendall test should be applied.	
<input type="checkbox"/> Check	If Mann-Kendall analysis was applied, are the graphs shown on a concentration-time diagram together with the data?	Graphs-groundwater concentration (or concentration ratios) versus time
<input type="checkbox"/> Check	Have geological cross sections with depth of contamination been prepared along site and across site?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall
<b>Risk</b>		
<input type="checkbox"/> Check	Has Short term vapor emission (including methane) from LNAPL, sheens, water, and ignition of vapor been investigated?	groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
<input type="checkbox"/> Check	Has long-term vapor emission/intrusion into overlying or nearby buildings, and vapor migration into onsite or offsite utility corridors or preferential pathways been investigated?	groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
<input type="checkbox"/> Check	Has migration of LNAPL into surface waters, storm drains, or other preferential pathways been investigated?	LNAPL footprint & groundwater COPC maps, preferential pathway maps
<input type="checkbox"/> Check	Has groundwater contamination and potential offsite migration onto nearby properties or surface water habitats been investigated?	LNAPL footprint & groundwater COPC maps, preferential pathway maps
<input type="checkbox"/> Check	Has protection of onsite or offsite workers or populations during construction been addressed	groundwater volatile COC maps, vapor maps, preferential pathway maps
<input type="checkbox"/> Check	Is there an increased risk in methane accumulation due to onsite liners and potentially lateral migration of vapors & methane	groundwater and vapor methane maps or graphs through time
<b>Remediation Considerations</b>		
<input type="checkbox"/> Check	Were source zones targeted for remediation	Map of remediation features, LNAPL footprint maps;
<input type="checkbox"/> Check	Were high permeability zones targeted for LNAPL extraction	Profiles along site and across site
<input type="checkbox"/> Check	Was the ROI as determined through pilot test sufficient to affect and extract the free LNAPL.	Map of remediation features, LNAPL footprint maps;
<input type="checkbox"/> Check	Did remediation system target the correct depth (E.g. vadose zone or saturated zone)	Profiles along site and across site. LNAPL footprint Maps
<input type="checkbox"/> Check	Has been demonstrated that MNA and NSZD is occurring.	MNA parameter maps & graphs
<input type="checkbox"/> Check	If MNA and NSZD is occurring- have degradation rates been determined?	
<input type="checkbox"/> Check	Have remediation timeframes been established for all proposed remedial options (default "reasonable timeframe" is 30 years)	Table remediation timeframes
<input type="checkbox"/> Check	Have remedial endpoints been established for each evaluated remediation option	Table remediation endpoints
<input type="checkbox"/> Check	If a remediation system was turned off- was investigated if rebound conditions occurred?	LNAPL footprint maps or graphs of LNAPL thickness variation through time for the same DTW; Graphs of concentration variations through time

Included ?	Item	Reference
<b>Maps/Profiles</b>		
<input type="checkbox"/> Check	Site Location	
<input type="checkbox"/> Check	Current And Historical Site Features with the following:	
<input type="checkbox"/> Check Box 1	Pipeline, USTs, ASTs, Oil/Water Separators, Tanker Truck Loading Racks, Tank Farm Walls (include content by year & capacity)	
<input type="checkbox"/> Check Box 1	Utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways	
<input type="checkbox"/> Check Box 1	Areas of current/historical pavement (asphalt, concrete) and or other surface covers such as liners?	
<input type="checkbox"/> Check Box 1	Areas excavated, remediated, locations of remediation features and radius of influence of remediation features (as determined by pilot tests preferentially or from specs if necessary)	
<input type="checkbox"/> Check	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall	
<input type="checkbox"/> Check	Product Occurrence -Different types based on observations of color, viscosities etc.	
<input type="checkbox"/> Check	Different types of LNAPL encountered in soil and groundwater (e.g. based on field observations-color, viscosity; different age based on age markers such as MTBE & lead in gasoline or sulfur in diesel)	
<input type="checkbox"/> Check	COCs above EALs in soil, groundwater and soil vapor maps (soil by DU; gw and sv contour maps)	
<input type="checkbox"/> Check	COPCs (or COPC ratios) that are indicators of different sources (e.g. MTBE, Ethanol, lead)- soil, sv, gw (contour maps)	
<input type="checkbox"/> Check	COPCs in groundwater or vapor (contour maps) that are indicators of residual sources (e.g.,less mobile COPC such as naphthalene, xylene) or COPCs/parameters indicating residual sources (e.g. methane or other anaerobic degradation products; low pH conditions, low oxygen zones, areas of high conductivity, thermal anomalies; low MTBE/TBA zones, high TPH-d SGC/TPH-d areas)	
<input type="checkbox"/> Check	Groundwater gradients at highest high tide and lowest low tide	
<input type="checkbox"/> Check	LNAPL footprint maps at maximum LNAPL thickness (lowest water level for unconfined, highest water level for confined conditions) through time.	
<input type="checkbox"/> Check	Free LNAPL and residual LNAPL map in 3 D (Maps & profiles)	
<input type="checkbox"/> Check	Redox zones (contours) based on groundwater MNA parameters (Methane, sulfate/sulfide/nitrate/Fe2+, Mn2+) and/or physical parameters (e.g., pH, redox potential, heat, conductivity)	
<input type="checkbox"/> Check	Methane Vapor Data	
<input type="checkbox"/> Check	LNAPL Gradient Maps	
<b>Tables</b>		
<input type="checkbox"/> Check	Tank (UST/AST) contents and capacities	
<input type="checkbox"/> Check	PID Screening values	
<input type="checkbox"/> Check	Release Sources, Years, and Volumes	
<input type="checkbox"/> Check	LNAPL Thickness Data with Date, DTW and DTP	
<input type="checkbox"/> Check	Soil Data	
<input type="checkbox"/> Check	Vapor Data (including methane, H2S, CO2, and O2 Data)	
<input type="checkbox"/> Check	Groundwater Data with Date, Time, and DTW	
<input type="checkbox"/> Check	Lag times for tides per well	
<b>Graphs</b>		
<input type="checkbox"/> Check	LNAPL thickness variations vs. DTW	
<input type="checkbox"/> Check	COC variations with DTW	

Checklist for More Complex Sites (Tier II)

Included ?	Item	Reference
<input type="checkbox"/> Check	Groundwater concentration graphs versus time with water table versus time and/or rainfall data versus time	
<input type="checkbox"/> Check	Methane conc/ in groundwater and vapor through time	
<input type="checkbox"/> Check	LNAPL thickness variations vs time at same DTW	
<b>Appendices</b>		
<input type="checkbox"/> Check	Laboratory Reports	
<input type="checkbox"/> Check	TPH chromatograms (TPH-g, TPH-d, and TPH-o) for soil, groundwater, vapor and LNAPL	
<input type="checkbox"/> Check	Boring Logs & Well Installation Logs with soil description, odor & staining description	
<input type="checkbox"/> Check	Photo Logs	

# **Tier III Checklist**



## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<b>Site Name:</b>		
<b>Site Setting (Target= identification of receptors and preferential pathways, Tier categorization)</b>		
<input type="checkbox"/> Check	Are properties surrounding the site described?	
<input type="checkbox"/> Check	Is zoning described?	
<input type="checkbox"/> Check	Are current & historical site use described?	
<input type="checkbox"/> Check	Are nearby surface water described and the distance to these surface waters?	
<input type="checkbox"/> Check	Is groundwater use & classification described and distance to the closest drinking water well?	
<input type="checkbox"/> Check	Is determined if site is located above or below UIC line ?	
<input type="checkbox"/> Check	Are current & historical site features mentioned and shown?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are any buildings used on site or is known where buildings will be placed in the future?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are contents, capacities of past and present storage containers described?	Map Current And Historical Site Features- Table - container/AST/UST number with contents and capacities by year
<input type="checkbox"/> Check	If Tank Farm Walls are present- Is described how far they reach into groundwater?	Map -Current And Historical Site Features
<input type="checkbox"/> Check	Are there utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways	Map-Utility Corridors & Preferential Pathways
<input type="checkbox"/> Check	Is described what the onsite surface cover is (soil, asphalt, concrete, liners) ?	Map -Current And Historical Site Features/Surface Cover
<input type="checkbox"/> Check	Have field observations been recorded (odor, staining, free product/sheen observations, PID readings)?	Table PID screening values/Boring Logs; Map of Product Observations
<input type="checkbox"/> Check	Has geology and permeability been described	Profiles -along site and across site
<input type="checkbox"/> Check	Is described if any areas were excavated or where remediation features are located and what the radius of influence is (as determined by pilot tests preferentially or from specs if necessary)	Map- Remediation Features/Remedial Excavation Features
<b>LNAPL Characteristics</b>		
<input type="checkbox"/> Check	Is the type of product released described, the year when released , and the release volume?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Is determined if product released has high or low viscosity?	
<input type="checkbox"/> Check	Has been identified if there has been one or multiple releases/LNAPL plumes?	Table of Release Sources, Years, and Volumes
<input type="checkbox"/> Check	Have different types of product been identified in the field indicating different/multiple releases?	Map of different type of LNAPL encountered in soil and groundwater (e.g. based on field observations-color, viscosity)
<input type="checkbox"/> Check	Have LNAPL, soil, groundwater, and/or vapor data been evaluated regarding source material?	Maps of COC and COPC that indicate different sources or source location
<input type="checkbox"/> Check	Have potentially very mobile (polar) COCs be identified (e.g., MTBE, fuel oxygenates)?	Maps of mobile COPCs on groundwater
<input type="checkbox"/> Check	Have potentially very volatile COCs be identified?	Maps of volatile COPCs in vapor
<input type="checkbox"/> Check	Has type or "aged" character of LNAPL been defined in any other way if release time is unknown? (e.g., lead in gasoline, MTBE or other oxygenates, sulfur content, different additives, viscosity, fingerprint analysis)	Maps of "age"-defining COPCs

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<b>Characterization of LNAPL in Dynamic Environment</b>		
<b>(Providing Context And Understanding What Drives LNAPL/Contaminant Distribution)</b>		
<input type="checkbox"/> Check	Has the relationship between LNAPL and water table change (tidal/seasonal) and COC concentration in groundwater and water table been investigated (e.g., tapping of shallow sources)? Has at key locations been determined if groundwater is under confined or unconfined conditions?	Graphs of LNAPL thickness and COC concentrations in groundwater vs. water table
<input type="checkbox"/> Check	Has extent of LNAPL contamination in soil below the water table been explored (trapped LNAPL)?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has a tidal study been conducted (time lag of tidal change at each well compared to coastal water)?	Map with lag time or table with lag time
<input type="checkbox"/> Check	Have LNAPL readings been systematic collected at the same stage of the tide, accounting for lag of time of tidal influence distant from the coast?	
<input type="checkbox"/> Check	Have data "outliers" been investigated and explained? (e.g., is there another evidence indicating a release, is there indication of rapid dewatering during sampling or was the water level unusually high so that a shallow source may have been tapped)?	
<input type="checkbox"/> Check	Do plots of concentrations ratios in groundwater with the same denominator indicate mixing of different groundwater plumes (different releases)?	Graphs of concentration ratios with same denominator
<input type="checkbox"/> Check	Has the groundwater gradient been determined at high and low tide and been corrected for the presence of free product?	Maps of groundwater gradients
<input type="checkbox"/> Check	Has the LNAPL composition been analyzed (Forensic/Fingerprint Analysis)?	Appendix Reports of LNAPL composition and chromatograms or maps and composition by location
<b>LNAPL plume delineation and Determination of Source Zones</b>		
<input type="checkbox"/> Check	Has the extent of free product (Free product footprint) been determined at maximum free product level (e.g., for unconfined situations lowest water level, confined at highest water level)?	LNAPL Footprint Maps
<input type="checkbox"/> Check	Has the extent of residual LNAPL been determined laterally and vertically and displayed together with LNAPL occurrences in soil & gw? Determination of LNAPL in 3-D from combined data of lowest & highest water level, staining and other field observations)	LNAPL Footprint and residual LNAPL Maps & Profiles, PID tables, field observations (Appendix)
<input type="checkbox"/> Check	Has the LNAPL extent been determined by any of the following: LIF/MIP/geophysical means/fluorescence paper test/tracer tests/ borehole geophysical log? State which  _____	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has potential offsite and onsite migration been discussed?	
<input type="checkbox"/> Check	Has the mass of LNAPL (free and residual) been estimated (e.g. by using concentrations per volume/unit area)?	
<input type="checkbox"/> Check	Has been determined if LNAPL is mobile? If it is mobile- is it also migrating?	LNAPL Footprint maps compared through time at same water level.

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<input type="checkbox"/> Check	Have all available data been combined to show LNAPL distribution (free and residual product) and been easily displayed on a map (free product, odor & staining observation, glove tests, paper towel tests, TPH concentrations and calculated saturation percentages, sheen observations, different types of products identified by color or viscosity)	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has extent of LNAPL in soil (free product plus residual LNAPL) been extrapolated to shallow depth at source container?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has deepest extent of LNAPL occurrence been determined below water table and LNAPL extent been extrapolated to at least lowest stand of water level in saturated zone?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall. Maps- Free product and residual LNAPL
<input type="checkbox"/> Check	Has the largest extent of the groundwater plume been determined based on high mobility contaminants (e.g., ethanol, MTBE, benzene)?	Contour Maps- COC in groundwater & COCs in vapor
<input type="checkbox"/> Check	Have source areas been identified for secondary groundwater and vapor plumes? (e.g., by mapping low(er)-mobility COCs in groundwater such as TPH-g/d/o, naphthalene, X, E, 1-Methylnaphthalene, 2-Methylnaphthalene)	Maps- COC in groundwater & COCs in vapor
<input type="checkbox"/> Check	Have groundwater field data (physical water quality data) been determined and calibrated to determine redox situation and been displayed on a map? (e.g. dissolved oxygen, pH, conductivity, or redox potential)? Low DO, high conductivity, and change in pH may indicate source zones.	Redox zone or physical parameters map.
<input type="checkbox"/> Check	Have MNA groundwater data be obtained (methane, Mn <sup>2+</sup> , Fe <sup>2+</sup> , sulfate, sulfide, nitrate, carbonate) to determine biodegradation presence, redox, and source zones? More reducing (e.g., methanogenic) areas indicate proximity to source areas and potential vapor intrusion hazard areas.	Redox zone or physical parameters map.
<input type="checkbox"/> Check	Have TPH-d SGC/TPH-d SGC ratios been displayed on a map. High TPH-d SGC/TPH-d SGC indicate proximity to LNAPL source if not affected by interferences.	Groundwater concentrations (or concentration ratios) contour map
<input type="checkbox"/> Check	Is there any other evidence for the presence of methanogenic zones (e.g. low MTBE/TBA) ratios?	Groundwater Concentrations (or concentration ratios) map
<input type="checkbox"/> Check	Have TPH-Chromatograms been submitted that could indicate interferences and provide information about degradation? (e.g., production of low C range aliphatics under methanogenic conditions)?	Appendix Chromatograms
<input type="checkbox"/> Check	Has the extent and behavior of mobile versus less/non-mobile compounds in groundwater been evaluated (e.g., B/X or B/naphthalene ratios B/TPH-g ratios with time and level of water)?- less mobile COCs are typically closer to the source and relatively more enriched with time; enhanced mobility at high water levels could indicate dissolution of shallow source or a new release- this should be distinguished	Groundwater Concentrations (or concentration ratios) contour map or graphs

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<input type="checkbox"/> Check	Have groundwater concentration maps been submitted that include concentrations at effective saturation levels for those wells that contained free product and were not sampled for groundwater?	Groundwater Concentration contour maps or graphs
<input type="checkbox"/> Check	Have vapor data been collected that could indicate the location of the main LNAPL mass (source) and been displayed on a map?	Vapor concentration contour maps
<b>LNAPL Mobility/Plume Stage</b>		
<input type="checkbox"/> Check	Have high permeability lithologies or zones been identified (e.g. fractured rock, gravel, coralline lithologies, lava tubes etc.)?	
<input type="checkbox"/> Check	Has LNAPL thickness and presence/absence in wells been shown at similar water table levels for different years?	LNAPL Footprint Maps
<input type="checkbox"/> Check	Have LNAPL gradients and water table gradients been determined for the same data set for different years?	LNAPL Gradient Maps
<input type="checkbox"/> Check	Have areas been identified where LNAPL is locally mobile (e.g., during tidal/seasonal changes) versus laterally mobile (migrating)?	LNAPL Footprint Maps
<input type="checkbox"/> Check	Has conductivity/transmissivity been determined using baildown or pump tests or other (petrophysical) tests?-If yes, has high/low water level at time of sampling been determined to place results into context of a dynamic environment?	Petrophysical results maps; tables,Appendix
<input type="checkbox"/> Check	Has conductivity/transmissivity been determined using residual or lab petrophysical tests?	Petrophysical results maps, tables,Appendix
<input type="checkbox"/> Check	If lab petrophysical tests have been conducted- were samples collected from enough boring locations and situations to be representative of the whole site?	Petrophysical results maps,tables, Appendix
<input type="checkbox"/> Check	Have samples for geophysical testing been adequately collected to minimize loss of fluids during retrieval?	
<input type="checkbox"/> Check	Is explained how the boring locations for petrophysical testing were determined?	
<input type="checkbox"/> Check	Have pore saturations been determined using TPH concentrations?	Petrophysical results maps, tables
<input type="checkbox"/> Check	If fluid saturations have been determined from TPH concentrations were enough and representative samples collected (e.g., MI samples)?	
<input type="checkbox"/> Check	Has the plume stage been defined? <span style="float: right;">How?</span>	
<input type="checkbox"/> Check	Has been proven that the release is not ongoing?	Groundwater concentration (and concentration ratios maps)
<input type="checkbox"/> Check	Has movement along potential preferential pathways been shown to not occur (e.g. no intersection of LNAPL footprint with preferential pathways, no product observations in preferential pathways or outfalls).	Preferential pathways (utility) Map and LNAPL footprint map, Photographs
<input type="checkbox"/> Check	Do dissolved concentrations decrease as shown in graph if COC versus time?	Graphs-groundwater concentration (or concentration ratios) versus time

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<input type="checkbox"/> Check	If statistical analysis was applied (aka Mann-Kendall) to show stable/decreasing/increasing conc., were data points excluded as "outliers"? If so, it needs to be explained why and what likely caused the deviation, so that a potential release causing high conc. won't be ignored. Note that if seasonal variations are identified, the seasonal Mann-Kendall test should be applied.	
<input type="checkbox"/> Check	If Mann-Kendall analysis was applied, are the graphs shown on a concentration-time diagram together with the data?	Graphs-groundwater concentration (or concentration ratios) versus time
<input type="checkbox"/> Check	Have geological cross sections with depth of contamination been prepared along site and across site?	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall
<input type="checkbox"/> Check	Has the LNAPL velocity potential been determined?	LNAPL Velocity Potential Map
<b>Risk</b>		
<input type="checkbox"/> Check	Has Short term vapor emission (including methane) from LNAPL, sheens, water, and ignition of vapor been investigated?	groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
<input type="checkbox"/> Check	Has long-term vapor emission/intrusion into overlying or nearby buildings, and vapor migration into onsite or offsite utility corridors or preferential pathways been investigated?	groundwater volatile COC maps, vapor maps, preferential pathway/utility (electrical) maps
<input type="checkbox"/> Check	Has migration of LNAPL into surface waters, storm drains, or other preferential pathways been investigated?	LNAPL footprint & groundwater COPC maps, preferential pathway maps
<input type="checkbox"/> Check	Has groundwater contamination and potential offsite migration onto nearby properties or surface water habitats been investigated?	LNAPL footprint & groundwater COPC maps, preferential pathway maps
<input type="checkbox"/> Check	Has protection of onsite or offsite workers or populations during construction been addressed	groundwater volatile COC maps, vapor maps, preferential pathway maps
<input type="checkbox"/> Check	Is there an increased risk in methane accumulation due to onsite liners and potentially lateral migration of vapors & methane	groundwater and vapor methane maps or graphs through time
<b>Remediation Considerations</b>		
<input type="checkbox"/> Check	Were source zones targeted for remediation	Map of remediation features, LNAPL footprint maps;
<input type="checkbox"/> Check	Were high permeability zones targeted for LNAPL extraction	Profiles along site and across site
<input type="checkbox"/> Check	Was the ROI as determined through pilot test sufficient to affect and extract the free LNAPL.	Map of remediation features, LNAPL footprint maps;
<input type="checkbox"/> Check	Did remediation system target the correct depth (E.g. vadose zone or saturated zone)	Profiles along site and across site. LNAPL footprint Maps
<input type="checkbox"/> Check	Has been demonstrated that MNA and NSZD is occurring.	MNA parameter maps & graphs
<input type="checkbox"/> Check	If MNA and NSZD is occurring- have degradation rates been determined?	
<input type="checkbox"/> Check	Have remediation timeframes been established for all proposed remedial options (default "reasonable timeframe" is 30 years)	Table remediation timeframes
<input type="checkbox"/> Check	Have remedial endpoints been established for each evaluated remediation option	Table remediation endpoints
<input type="checkbox"/> Check	If a remediation system was turned off- was investigated if rebound conditions occurred?	LNAPL footprint maps or graphs of LNAPL thickness variation through time for the same DTW; Graphs of concentration variations through time

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<b>Maps/Profiles</b>		
<input type="checkbox"/> Check	Site Location	
<input type="checkbox"/> Check	Current And Historical Site Features with the following:	
<input type="checkbox"/> Check	Pipeline, USTs, ASTs, Oil/Water Separators, Tanker Truck Loading Racks, Tank Farm Walls (include content by year & capacity)	
<input type="checkbox"/> Check	Utility corridors, internal/external storm drain features, remediation trenches/lines, or other potential preferential pathways	
<input type="checkbox"/> Check	Areas of current/historical pavement (asphalt, concrete) and or other surface covers such as liners?	
<input type="checkbox"/> Check	Areas excavated, remediated, locations of remediation features and radius of influence of remediation features (as determined by pilot tests preferentially or from specs if necessary)	
<input type="checkbox"/> Check	Profiles - Along site and across sites, showing lithology, water table, and depth of free and residual/trapped LNAPL, extent of teank farm wall	
<input type="checkbox"/> Check	Product Occurrence -Different types based on observations of color, viscosities etc.	
<input type="checkbox"/> Check	Different types of LNAPL encountered in soil and groundwater (e.g. based on field observations-color, viscosity; different age based on age markers such as MTBE & lead in gasoline or sulfur in diesel)	
<input type="checkbox"/> Check	COCs above EALs in soil, groundwater and soil vapor maps (soil by DU; gw and sv contour maps)	
<input type="checkbox"/> Check	COPCs (or COPC ratios) that are indicators of different sources (e.g. MTBE, Ethanol, lead)- soil, sv, gw (contour maps)	
<input type="checkbox"/> Check	COPCs in groundwater or vapor (contour maps) that are indicators of residual sources (e.g.,less mobile COPC such as naphthalene, xylene) or COPCs/parameters indicating residual sources (e.g. methane or other anaerobic degradation products; low pH conditions, low oxygen zones, areas of high conductivity, thermal anomalies; low MTBE/TBA zones, high TPH-d SGC/TPH-d areas)	
<input type="checkbox"/> Check	Groundwater gradients at highest high tide and lowest low tide	
<input type="checkbox"/> Check	LNAPL composition (e.g. Pie charts) by location	
<input type="checkbox"/> Check	LNAPL footprint maps at maximum LNAPL thickness (lowest water level for unconfined, highest water level for confined conditions) through time	
<input type="checkbox"/> Check	Free LNAPL and residual LNAPL map in 3 D (Maps & profiles)	
<input type="checkbox"/> Check	Redox zones (contours) based on groundwater MNA parameters (Methane, sulfate/sulfide/nitrate/Fe2+, Mn2+) and/or physical parameters (e.g., pH, redox potential, heat, conductivity)	
<input type="checkbox"/> Check	Methane Vapor Data	
<input type="checkbox"/> Check	LNAPL Gradient Maps	
<input type="checkbox"/> Check	Petrophysical test results maps	
<input type="checkbox"/> Check	LNAPL Velocity Potential	
<input type="checkbox"/> Check	Tide lag times for each well	
<b>Tables</b>		
<input type="checkbox"/> Check	Tank (UST/AST) contents and capacities	
<input type="checkbox"/> Check	PID Screening values	
<input type="checkbox"/> Check	Release Sources, Years, and Volumes	

## LNAPL CSM Checklist for Complex Sites (Tier III)

Included ?	Item	Reference
<input type="checkbox"/> Check	LNAPL Thickness Data with Date, DTW and DTP	
<input type="checkbox"/> Check	Soil Data	
<input type="checkbox"/> Check	Vapor Data (including methane, H2S, CO2, and O2 Data)	
<input type="checkbox"/> Check	Groundwater Data with Date, Time, and DTW	
<input type="checkbox"/> Check	Lag times for tides per well	
<b>Graphs</b>		
<input type="checkbox"/> Check	Mixing graphs (e.g., groundwater concentration ratios indicating multiple LNAPL sources are mixing)	
<input type="checkbox"/> Check	LNAPL thickness variations vs. DTW	
<input type="checkbox"/> Check	COC variations with DTW	
<input type="checkbox"/> Check	Groundwater concentration graphs versus time with water table versus time and/or rainfall data versus time	
<input type="checkbox"/> Check	Methane conc/ in groundwater and vapor through time	
<input type="checkbox"/> Check	LNAPL thickness variations vs time at same DTW	
<b>Appendices</b>		
<input type="checkbox"/> Check	Laboratory Reports	
<input type="checkbox"/> Check	TPH chromatograms (TPH-g, TPH-d, and TPH-o) for soil, groundwater, vapor and LNAPL	
<input type="checkbox"/> Check	Boring Logs & Well Installation Logs with soil description, odor & staining description	
<input type="checkbox"/> Check	Photo Logs	
<input type="checkbox"/> Check	Baildown test description	
<input type="checkbox"/> Check	All input parameters used in modeling	