Answers to Frequently Asked Questions
About Managing Risk at LNAPL Sites

INTRODUCTION

Petroleum liquids are a basic building block of our modern lives. Uses include fuels, lubricants, and the raw material for manufactured products. Current consumption in the United States is estimated at 840 million gallons per day. Total use over the last 100 years is on the order of one million times 10 million gallons (www.eia.doe.gov). All of this has brought great convenience to our lives. Unfortunately, a by-product has been the inadvertent release of petroleum liquids. Fortunately, releases represent a very small fraction of total use and improvements in infrastructure have dramatically reduced the potential for future releases. Nevertheless, a result of our utilization of petroleum liquids is a legacy of soil and groundwater impacted by petroleum liquids.

Over the last 30 years recognition of the need for better environmental stewardship has driven rapid evolution of science and technology associated with managing releases of petroleum liquids. This is reflected in a steady stream of journal articles, books, short courses, conferences, and web pages devoted to the topic. So much information now exists that it is challenging to remain up-to-date. The intent of this document is to provide a concise overview of current knowledge through the format of "Frequently Asked Questions." Each question is first addressed with a short answer. This is followed by a more detailed answer in a shaded box area for those who wish to know more.

As you read the questions and answers presented here, it is important to remember that overall site management involves decision-making not only about the petroleum liquid itself, but also consideration of other affected media and exposure pathways (e.g., dissolved hydrocarbon plumes and vapor migration to enclosed spaces). This paper assumes that the reader has a working knowledge of how dissolved and vapor phase plumes are generated from petroleum liquid source areas and how natural attenuation and other processes (natural and enhanced) limit their mobility and extent.

WHAT IS LNAPL?

LNAPL is a convenient label for petroleum liquids in soils and groundwater. The acronym stands for Light Nonaqueous Phase Liquid. "Light" highlights the fact that petroleum liquids are (with a few minor exceptions) less dense than water. "Nonaqueous" highlights the fact that petroleum liquids do not mix with water.

In more detail, LNAPLs are derived from crude oil. Common LNAPLs include fuels, lubricants, and chemical feed stock for manufacturing. From an environmental perspective, key features of LNAPL include:

1) LNAPLs are typically found at the top of groundwater zones. The buoyancy of LNAPL in water inhibits LNAPL migration into the groundwater zone.

2) When combined, LNAPL and water do not mix. They are immiscible. The net result is that subsurface LNAPL and water share pore space in soils and rock impacted by LNAPL. This "sharing of pore space" limits the mobility of LNAPL and complicates its recovery. **Recognizing LNAPL releases as a problem involving multiple fluid phases in pore space is essential to developing effective solutions for LNAPL releases.**

3) LNAPLs are composed of mixtures of organic molecules that are slightly soluble in water. Where LNAPL comes in contact with groundwater, trace to low percent concentrations of the organic compounds dissolve into it. This often results in exceedances of water quality standards close to releases. A benefit of low solubility is that loading to the environment is typically small and natural processes often attenuate contaminants of concern over small distances. A disadvantage of low solubility is that LNAPL can persist as a source of groundwater contamination for extended periods.

WHAT HAPPENS WHEN LNAPL IS RELEASED?

Released LNAPL migrates downward through the subsurface under the influence of gravity. Above the groundwater zone volatile LNAPL components separate into soil gas and form vapor plumes close to the release. The extent of vapor plumes is limited by natural *in situ* physical and biological processes (see Roggemans et al., 2001). Given a large enough release LNAPL will encounter the groundwater zone. At the groundwater zone LNAPL spreads laterally and begins to dissolve into groundwater. Once the surface LNAPL release ceases, subsurface spreading of LNAPL slows and ultimately stops. With time, plumes of petroleum molecules, dissolved in groundwater, form in the vicinity of the release and begin to migrate downstream. Typically these plumes are attenuated via biological processes over short distances (e.g., a few hundred feet, Wiedemeier et al., 1999). Over extended periods the most soluble compounds weather out of the LNAPL leaving behind a mixture of low solubility - high viscosity compounds.

Historically, a perspective held by many was that LNAPL releases could be conceptualized as adding oil to a tank with water in it. Oil would float above the water and cleanup would involve pumping out the LNAPL. The anticipated result was near complete LNAPL depletion. Building on decades of research in petroleum production and soil physics this conceptualization has been displaced by a more thoughtful understanding. We encourage readers to consider the following carefully as it is essential to managing LNAPL releases.

Everything below land surface can be described as porous media. Porous media consists of solids (e.g., soil grains) and void space (soil pores). Above the groundwater zone air coexists with water in the pore space. Water is preferentially attracted to the solids and forms a continuous coating ("wetting phase") around the soil grains and fills the smaller pore spaces. In doing this water occupies the margins of the pore space, leaving the remaining central portions filled with air (a non-wetting fluid). Figure 1 is a photograph of porous media that contains wetting and non-wetting fluids.
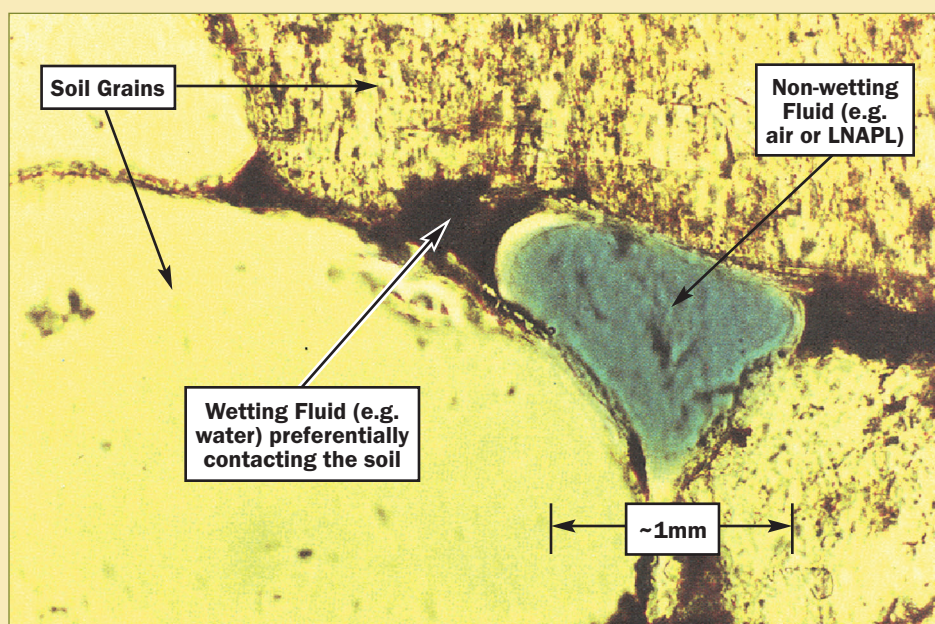

Figure 1 – Multiple fluids in the pore space of a granular porous media (From Wilson et al., 1990)

Released LNAPL flows downward through the interval above the groundwater zone as a non-wetting phase that partially displaces air. Water remains on the solids as a continuous wetting phase around the sediments. Given a release of sufficient volume, the LNAPL will reach the groundwater zone. Within the groundwater zone LNAPL displaces water from the interior of the largest pores. Selective entry of LNAPL into larger pores reflects the fact that it is easier for LNAPL to displace water from large pores than smaller pores. Initially, LNAPL occurs in the groundwater zone as a continuous network of interconnected pores that contain LNAPL. The LNAPL is surrounded by water that forms a continuous phase about the solids. This is illustrated in Figure 2 using an idealized pore network. Real porous media has a large range of pore sizes and consequently LNAPL is far less uniform than indicated in Figure 2.
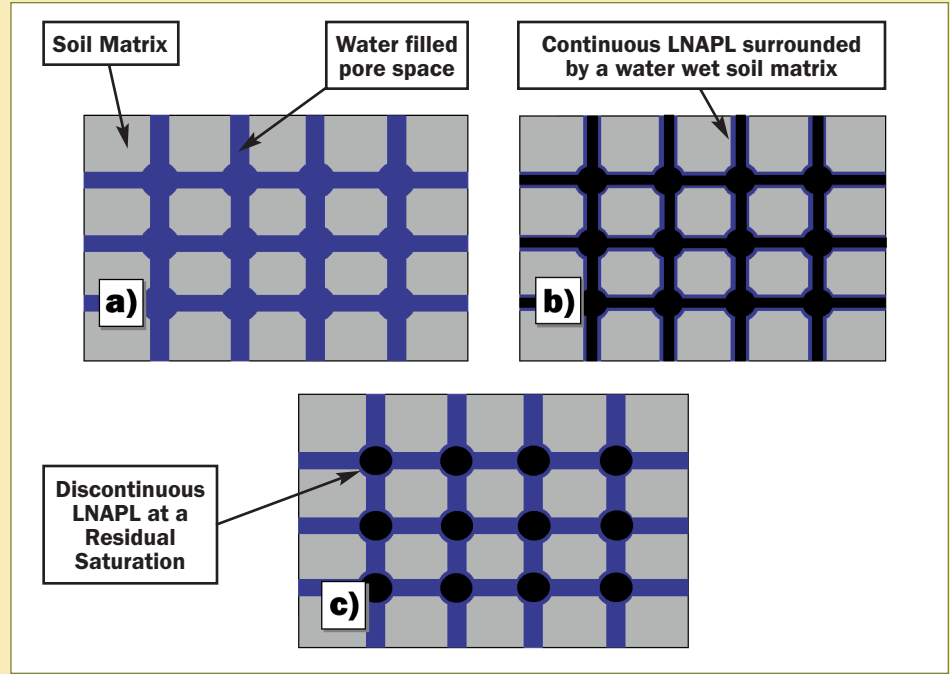
WHAT HAPPENS WHEN LNAPL IS RELEASED?

Figure 2 – Groundwater zone with continuous and discontinuous (residual) LNAPL occurrence in an idealized fracture network (After Wilson et al., 1990)

While the described system is complex, understanding it is essential to addressing the challenges posed by LNAPLs. Consequences include:

◆ **LNAPL does not float above groundwater** as suggested by the analogy of oil floating on water in a tank. Instead, as noted by David McWhorter[1], LNAPL rests like an iceberg in the sea, largely submerged. Movement of LNAPL is constrained by the pressures needed to displace water from the pores at the margins of the LNAPL.

◆ Water and LNAPL coexist in the pores under different pressures. The difference in pressure between the LNAPL (non-wetting phase) and water (wetting phase) is defined as capillary pressure. The difference in fluid pressures is shown in Figure 1 where the non-wetting phase (e.g., air or LNAPL) forms a convex surface pushing into the wetting phase (e.g., water). The greater the pressure in the non-wetting (e.g., LNAPL) the more fully the pore space is filled (saturated) by the non-wetting phase.

◆ Capillary pressure is a result of the two liquids (water and LNAPL) having different densities $[P_c = (\rho_{LNAPL} - \rho_{water})gh_{LNAPL}]$ (see footnote 2). This property plays a primary role in the distribution and potential mobility of LNAPL in groundwater.

◆ As LNAPL is depleted by dissolution or another removal mechanism, the fraction of pore space occupied by LNAPL (saturation) decreases. With depletion LNAPL flow paths become smaller and more tortuous. This reduces the ease with which LNAPL can move (mobility). Ultimately the LNAPL breaks into isolated blobs and ganglia that are discontinuous and immobile as a separate liquid phase (See Figure 2c). The saturation at which LNAPL is immobile is referred to as residual saturation.

Factors governing LNAPL dissolution into groundwater and partitioning into soil gas are discussed in subsequent text.

1) Professor Emeritus Colorado State University, Recipient of the National Ground Water Association's 2001 M.K. Hubbert Award.
2) P_c = Capillary Pressure, ρ_{LNAPL} = density of the LNAPL, ρ_{water} = density of the water, g = gravitational constant, h_{LNAPL} = vertical height of LNAPL.

WHAT MAKES CLEANUP OF LNAPL RELEASES SO CHALLENGING?

Experience of the last few decades has taught us:

1) Our best efforts often leave some LNAPL behind, and,

2) The remaining LNAPL often sustains exceedances of drinking water standards in release areas.

Entrapment of LNAPLs at residual saturations (as described above) is a primary factor constraining our success. Other challenges include fluctuating water table elevation, slow rates of LNAPL dissolution, high viscosity of some LNAPLs, the complexity of the subsurface geologic environment, buildings and equipment that limit access to the subsurface, and concentration goals that are often 3 to 5 orders of magnitude less than typical initial conditions within LNAPL zones.

David Miller[3] suggested that trying to clean up an aquifer is like trying to get all the soap out of a sponge. To take this further, cleaning up LNAPL is like soaking a sponge in oil, placing it in a dark room, and then trying to get it clean enough that one would drink the rinse water for the rest of your life. From a technical perspective, challenges include:

Entrapment of LNAPL at Residual Saturations – Removal of LNAPL results in invasion of water into the pore space. As this occurs LNAPL flow paths become smaller and more tortuous. This reduces the ability of the porous media to allow LNAPL to flow through it. Eventually enough LNAPL is removed that a continuous network for LNAPL flow no longer exists. The saturation at which LNAPL becomes discontinuous (and consequently immobile) is referred to as a residual saturation. The bottom line is that direct pumping of LNAPL results in decreasing recovery rates with time (making recovery more difficult with time) and, at best, fractional LNAPL depletion.

Fluctuating Watertable Elevations – Fluctuating watertable elevations reflect seasonal or tidal conditions or climatic cycles such as periods of above average precipitation or drought. Rising and falling watertable elevations spread LNAPL about the watertable. As this occurs, the mobility of the LNAPL, and the amount of LNAPL exposed to soil gases, changes. At high watertable elevations much of the LNAPL can be trapped as discontinuous blobs (residual saturation) below the watertable. At low watertable elevations trapped LNAPL can drain from the exposed unsaturated zone to form an LNAPL layer with greater mobility. As such, the efficacy of LNAPL depletion by pumping of fluids and/or soil gases will vary with periods of high and low watertable elevation.

Slow Rates of Dissolution – LNAPL is depleted by dissolving in groundwater and soil gas. Dissolution into groundwater is slow due to the low solubility of LNAPL in water and the slow flow of groundwater. Removal via soil gas is constrained by limited contact between LNAPL and soil gas (much of the LNAPL is submerged) and the limited circulation of air in subsurface porous media.

High Viscosity LNAPLs – Some LNAPLs (e.g., heating oil and crude oil) have viscosities 20 to 50 times greater than water. Where these LNAPLs occur in low permeability sediments, recovery by pumping can be very slow (e.g., like molasses in January). Furthermore, high viscosity LNAPL are typically composed of high boiling point compounds. These compounds have low solubility and volatility. Consequently, depletion via dissolution and/or volatilization can be slow.

Complexity of Setting – Natural geologic settings are often complex. So much so that two holes drilled within a few tens of feet of each other can indicate substantially different conditions. Site complexity is further increased by surface structures. Buildings, tanks, process units, utilities, and/or roadways often limit access for investigation and construction of recovery systems.

Stringent Goals – At many locations the ultimate goal is to return the groundwater quality in the release area to drinking water standards. In the case of benzene this can require reducing aqueous concentrations by three to five orders of magnitude. Near-term attainment of this goal often requires recovery of essentially all of the LNAPL (e.g., Sale and McWhorter, 2001, and Huntley and Beckett, 2002).

For all the reasons noted above, attainment of typical cleanup goals (e.g., drinking water standards) is not easy.

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3) Co-founder of Geraghty and Miller

I CAN MEASURE LNAPL IN A WELL AT MY SITE.
SHOULDN'T I BE ABLE TO PUMP IT OUT OF THE GROUND?

Historically it was widely thought that the thickness of LNAPL in a well was a direct indicator of the potential (and need) to recover LNAPL. This perception suffers from a long list of limitations. Porous media properties, natural layering of sediments, LNAPL physical properties, vertical hydraulic gradients, non-equilibrium conditions, and watertable fluctuations all create significant biases between LNAPL thickness in a well and the amount of recoverable LNAPL in an aquifer. Reflecting these limitations, alternative means of answering the question of "shouldn't I be able to pump it out of the ground" have been developed. These include models (e.g., Charbeneau et al., 1999), laboratory tests (described in Sale, 2001), field tests (described in Sale, 2001), and tabulations of input parameters for models (e.g., Aqui-Ver, Inc., in preparation).

In more detail, the relationship between LNAPL thickness in a well and the volume of LNAPL in formation is complex. Following Farr et al. (1990), Figure 3 considers a simple case in which LNAPL has migrated laterally into a uniform porous media where the watertable is stable. Panel 1 shows that LNAPL in the well extends below the LNAPL in the formation. Within this extension the pressure difference between the LNAPL in the well and the water in the formation is not large enough to push the water out of the formation (capillary pressure is less than displacement pressure). The extension of product in the well, below the elevation in the formation, increases as soils become finer and as the densities of the liquids becomes more similar.
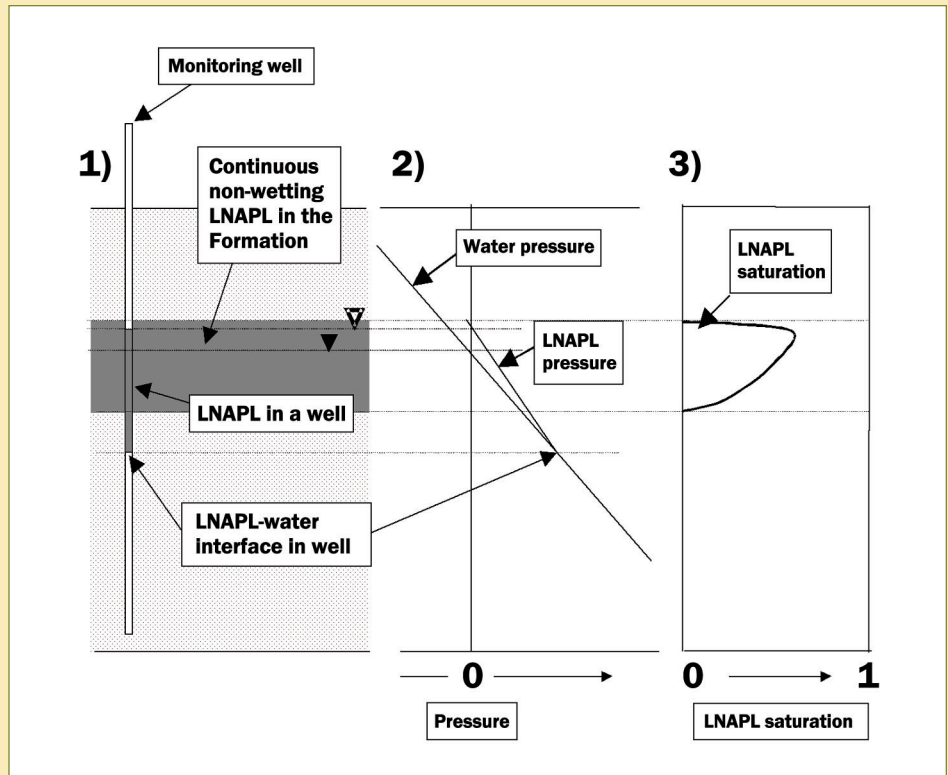

Figure 3 – Idealized conceptualization of LNAPL in a well and adjacent formation

Panel 2 shows pressure in the LNAPL and water to be equal at the LNAPL water interface in the well. Above this point the difference between LNAPL and water pressure increases. Note the slope of the LNAPL and water pressure lines are different because the fluids have different densities (Pressure = Fluid Density x Gravitational Coefficient x Height). As shown in Panel 3 the fraction of the pore space filled with LNAPL (saturation) changes vertically. Moving upward from the LNAPL water interface in the well the pressure difference between the LNAPL and water increases. As this occurs the LNAPL saturation increases. Decreasing LNAPL saturation at the top reflects the condition where air begins to occupy pore space along with LNAPL and water.

I CAN MEASURE LNAPL IN A WELL AT MY SITE.
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The ideal conditions identified in Figure 3 often don't exist. Potential variations are shown in Figure 4. Panel 1 illustrates a scenario where the monitoring well is completed into an underlying gravel with a lower hydraulic head. The low pressure in the underlying layer draws LNAPL down the well. At the extreme, this condition has caused as much as 30 feet of LNAPL to be present in a well where only a few feet of continuous LNAPL is present in the formation. Panel 2 shows a scenario where LNAPL is below a fine-grained soil layer. Pressure in the LNAPL is never great enough to displace water from the fine-grained sediments. Note: this same principle traps crude oil in natural petroleum reservoirs. The absence of resistance in the well results in LNAPL rising above the true elevation in the formation. Panel 3 considers LNAPL in a fine-grained silt or clay. LNAPL only occurs in sparse secondary features with large (relative) pore dimensions such as joints, sand seams, root casts or animal burrows. In this case the potential to recover LNAPL has little to do with the thickness in the well. This condition is commonly observed along the Gulf Coast of the United States and in glacial tills.
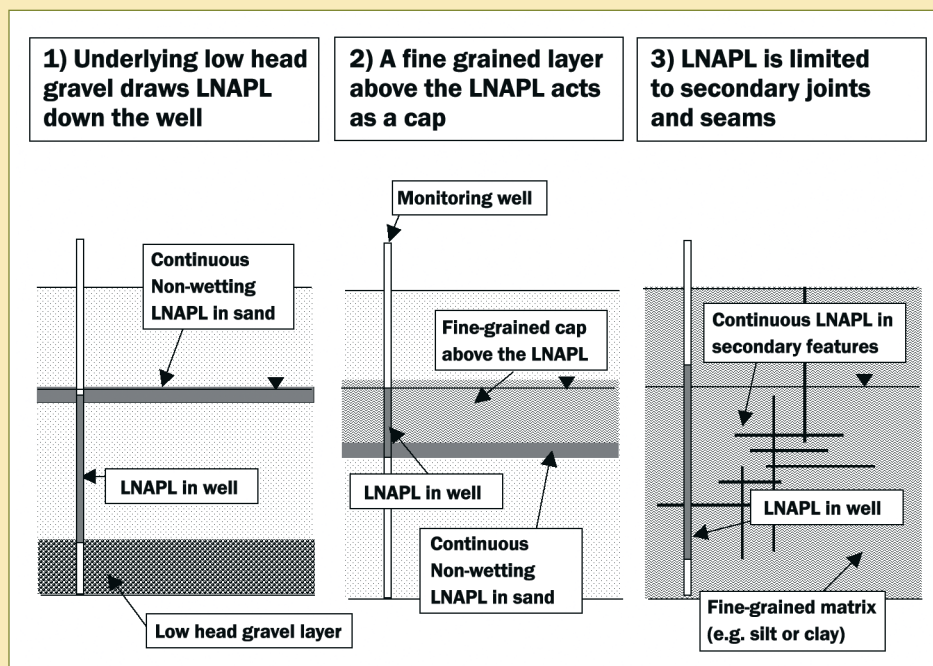

1) Underlying low head gravel draws LNAPL down the well

2) A fine grained layer above the LNAPL acts as a cap

3) LNAPL is limited to secondary joints and seams

Monitoring well

Continuous Non-wetting LNAPL in sand

LNAPL in well

Low head gravel layer

Fine-grained cap above the LNAPL

LNAPL in well

Continuous Non-wetting LNAPL in sand

Continuous LNAPL in secondary features

LNAPL in well

Fine-grained matrix (e.g. silt or clay)

Figure 4 − Conditions effecting thickness of LNAPL in wells

Charbeneau et al. (1999) and Charbeneau (2003) provide a spreadsheet model that addresses the recoverability of LNAPL for the ideal condition presented in Figure 2. Text and the spreadsheet are available at www.api.org/lnapl. For more complex situations it is often necessary to conduct baildown or pumping tests to evaluate LNAPL recoverability. These are methods are reviewed in Sale (2001).

WHAT DO I NEED TO KNOW ABOUT A SITE TO ESTIMATE WHETHER OR NOT LNAPL IS MOVING IN THE SUBSURFACE?

When LNAPL is observed in wells, a common concern is whether the LNAPL is moving. Typically, as long as an LNAPL release continues, LNAPL in the subsurface is moving. Once a release stops, the forces driving migration dissipate and the rate of LNAPL migration slows. With time the driving force becomes insufficient to drive further LNAPL movement. This occurs when the pressure in the LNAPL is not large enough to displace the water at the margin of the released LNAPL body. As noted by G.D. Beckett[4] the widely observed stability of dissolved BTEX (benzene, toluene, ethylbenzene, and xylene) plumes provides a strong basis for LNAPL being largely stable.

In more detail, the following can help resolve whether LNAPL is moving:

Active LNAPL migration is likely if:

◆ Ongoing LNAPL releases are known to exist (e.g., a chronic leak from a pipeline or tank).

◆ LNAPL is chronically discharging to surface water (e.g., seeps to surface water).

Active LNAPL migration is unlikely if:

◆ LNAPL pumping systems have been deployed through the area of concern and operated to a near zero LNAPL recovery rate. Near zero recovery rates from well-designed and operated recovery systems typically reflect depletion of LNAPL saturation to the point were the remaining LNAPL is largely present as a discontinuous immobile residual. Furthermore, it follows that if LNAPL is immobile under the large gradients imposed by pumping it is unlikely that the LNAPL will move (substantially) under smaller natural gradients.

◆ Dissolved phase BTEX plumes have been shown to be stable for an extended period of time. Again, following G. D. Beckett[4], stable BTEX plumes in groundwater require that the LNAPL is also stable.

While the above is useful for screening, it will not resolve conditions at all sites. In select cases more rigorous analyses may be needed. Typically these build on Darcy's Equation for flow in porous media. In words this can be stated as

LNAPL Seepage Velocity = (Conductivity to LNAPL) x (Driving Force)   (1)

Mathematically this can be written as

$$v_{LNAPL} = -\left(\frac{k k_{rLNAPL} \rho_{LNAPL} g}{\mu_{LNAPL} n S_{LNAPL}}\right)\left(\frac{dh_{LNAPL}}{dx}\right) \quad \text{(see footnote 5)} \qquad (2)$$

The terms in the first bracket on the right hand side describe the formation's capacity to conduct LNAPL. Methods for determining the first bracket terms are described later. The inputs in the second bracket describes the driving force. This information can be obtained using the elevation of the top of oil in three or more wells within a body of continuous LNAPL. When applying this technique one often finds that LNAPL moves far slower than groundwater at older releases. Recognizing groundwater flow to be slow (e.g., < 1 ft /day) LNAPL seepage velocities can be quite small (e.g., < 0.1 − 0.01 ft/day). On the other hand, observed migration rates from release points suggest that LNAPL may have moved faster than groundwater during the period(s) of active release. This would be consistent with large driving forces associated with LNAPL mounds beneath release points. Lastly, as shown in Equation (2), LNAPL seepage velocity is inversely proportional to viscosity.

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4) G.D. Beckett, San Diego State University.
5) v_{LNAPL} = seepage velocity of the LNAPL, k = permeability of the porous media, k_{rLNAPL} = relative permeability of the porous media to LNAPL, ρ_{LNAPL} = density of the LNAPL, g = gravitational constant, μ_{LNAPL} = viscosity of the LNAPL, n = porosity, S_{LNAPL} = fraction of the pore space filled with LNAPL, h_{LNAPL} = LNAPL head, and x = the direction of LNAPL flow.

THROUGH TIME, PRODUCTION FROM MY RECOVERY SYSTEM HAS DECAYED DOWN TO LEVELS THAT ARE SMALL RELATIVE TO INITIAL RATES. HOW DO I DECIDE WHEN TO STOP?

As LNAPL is depleted from subsurface releases it typically gets harder and harder to recover what remains. This leads to diminishing production with time and cumulative LNAPL recovery curves similar to that shown in Figure 5. In the case of direct pumping, LNAPL depletion causes water to invade the geologic formation containing the LNAPL. This reduces the formation's capacity to transmit LNAPL and slows flow to the recovery systems. The idealized physics of the problem indicate that it would take an infinite period of time to get to a zero recovery rate (Sale and Applegate, 1997). In the case of pumping soil gases, production removes the most volatile compounds first and reduces contact between LNAPL and soil gases. In either case recovery should continue only so long as what can be produced is significant relative to what remains. These ideas are developed in more detail below.
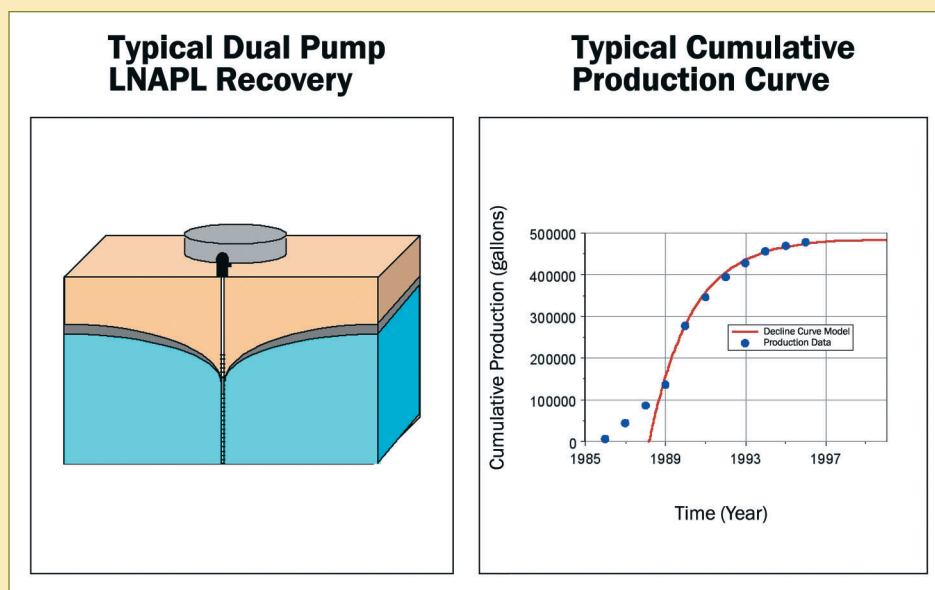

Figure 5 – Typical production curve

Where LNAPL is observed in wells a common measure is to pump it out. This can be accomplished using a wide range of techniques including bailing, dedicated skimming pumps, and simultaneous extraction of LNAPL, groundwater and/or soil gas. The volume of LNAPL recovered through such actions is highly variable (e.g., one gallon to thousands of gallons). Variability reflects volume of LNAPL released and hydrogeologic conditions. Despite variability, attributes common to most LNAPL depletion or removal schemes include the following:

◆ The volume recovered is often substantially less than what was released (e.g., <1/2). In large part this is due to LNAPL becoming trapped as a discontinuous residual as it is depleted from the formation. Other factors constraining recovery are geologic heterogeneity, mobility that decays with production, and physical access limitations.

◆ With time recovery rates decay to levels that are inconsequential relative to what remains. For example, the LNAPL recovery system shown in Figure 5 will at best produce 1/2 of the total LNAPL present. With this, the amount of LNAPL that can be produced through extended operation (e.g., beyond 95% of the ultimate recovery) will not substantially alter the total amount of LNAPL (mobile and residual) left in place.

◆ Due to the complex relationships between the thickness of product in a well and the volume of recoverable oil in the formation, LNAPL often remains in wells after production rates have diminished to inconsequential rates. As the height of continuous LNAPL in the formation goes to zero the thickness of LNAPL in wells can range from inches to feet depending on the characteristics of the porous media adjacent to the well (See Figures 3 and 4).

One approach to determining how much LNAPL will remain is decline curve analysis. This is described in Sale (2001). This text is available at www.api.org/lnapl.

HOW CAN I OBTAIN INPUT TO MODELS THAT ESTIMATE LNAPL MOBILITY AND RECOVERABILITY?

Many LNAPL problems can be analyzed using mathematical models. Necessary inputs can be obtained by conducting site-specific studies or by using typical values for known conditions. To facilitate use of models API produced *Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and* *Recovery Models* (Sale, 2001), and *Input Database for LNAPL Modeling* (Aqui-Ver, Inc., in preparation). These products can be found at www.api.org/lnapl.

I'VE COLLECTED VALUES FOR THE KEY INPUT PARAMETERS. HOW DO I USE THE DATA TO ESTIMATE LNAPL RECOVERABILITY AND MOBILITY?

A number of tools are presently available to develop *a priori* assessments of how LNAPL management strategy will affect the ultimate distribution of LNAPL. These tools range from simple spreadsheets to complex three dimensional petroleum reservoir simulators. Which tool should be used in a given situation is largely a function of objectives. As such a logical first step is to resolve objectives. Common issues include:

◆ How much further can LNAPL migrate given current or plausible future conditions?
◆ How much LNAPL will remain after implementing a given recovery scenario?

Next, a conceptual site model should be developed that encompasses the context in which the above questions need to be addressed. Lastly, select and apply one of the available models. Start with simple models and proceed to more complex models only if the need arises.

A good place to start is the spreadsheet models described in "Free-Product Recovery of Petroleum Hydrocarbon Liquids" (Charbeneau et al., 1999 and Charbeneau, 2003). The Microsoft® Excel spreadsheets themselves can be downloaded at www.api.org/lnapl.

With the spreadsheets one can calculate the vertical distribution of LNAPL in the subsurface given a product thickness in a well, LNAPL properties, and physical properties of the porous media. This calculation can be used to estimate the volume of LNAPL present and capacity of the subsurface to conduct LNAPL (See Figures 6a and 6b). Using this output one can estimate the volume of recoverable LNAPL via pumping and (using Equation (2)) the potential seepage velocity of the LNAPL.

Another part of the spreadsheet utility can be used to calculate LNAPL recovery rates, cumulative LNAPL production as a function of time, and remaining LNAPL as a function of time. As an example Figure 7 plots cumulative production versus time. Using this tool one can compare different scenarios of hydraulic LNAPL depletion.
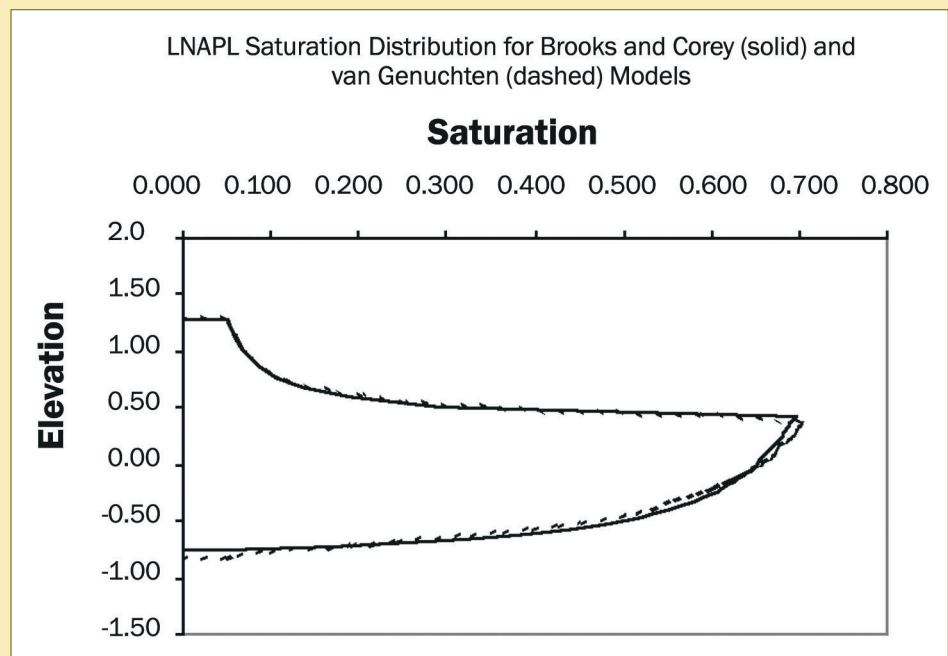

Figure 6a − Estimates of the amount of LNAPL present in terms of saturation

I'VE COLLECTED VALUES FOR THE KEY INPUT PARAMETERS.
HOW DO I USE THE DATA TO ESTIMATE LNAPL RECOVERABILITY AND MOBILITY?

Continued from page 10

In addition there are a number of numerical models that can be employed. Examples include UTCHEM (Delshad, 1996) and ARMOS (ES&T Software Ltd., 1988). These models are far more complex than the spreadsheet models, require more rigorous inputs, and are best run by individuals with significant experience with multiphase flow modeling. As a cautionary note it should be recognized that the complexity of these models does not necessarily guarantee better answers.

LNAPL Relative Permeability, kro, for Brooks and Corey (solid) and van Genuchten (dashed) Models
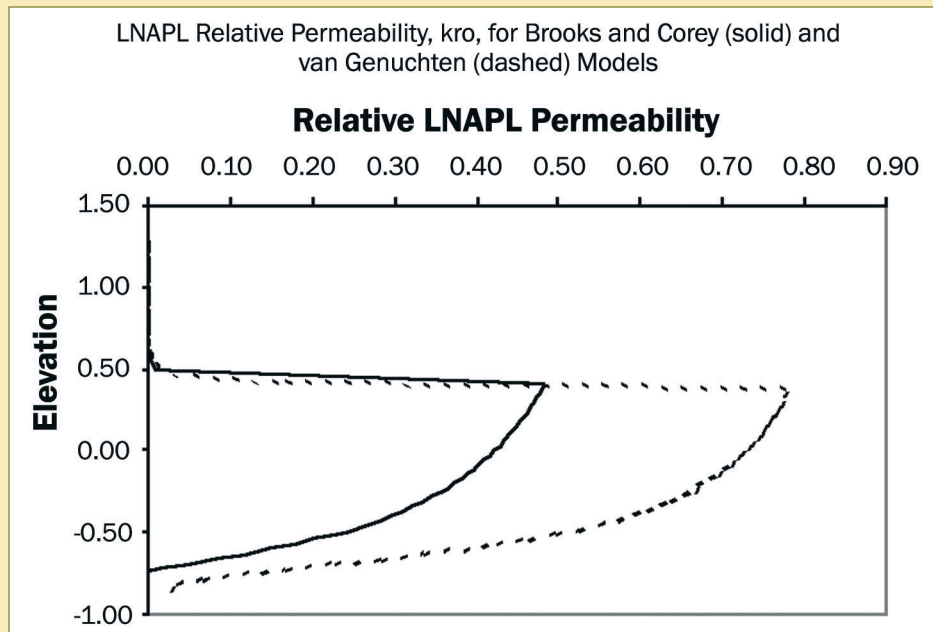
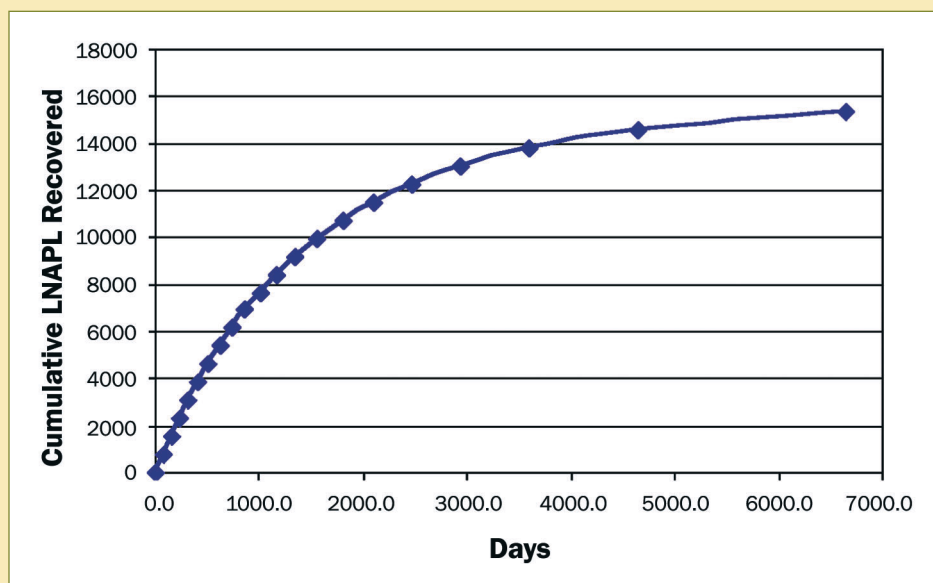**Figure 6b –** Estimates of the relative permeability of LNAPL

Figure 7 – Cumulative LNAPL recovery as a function of time

UNDER THE BEST OF CIRCUMSTANCES, I THINK I CAN REMOVE 25% OF THE LNAPL. HOW CAN I DETERMINE WHAT EFFECT THIS WILL HAVE ON THE DISSOLVED PLUME OVER SHORT AND LONG TIME FRAMES?

One of the most critical issues at LNAPL sites is how a given amount of LNAPL depletion will affect groundwater quality through time. The answer to this question depends on the size of the release, hydrogeologic conditions, and the type of LNAPL released. At a cursory level we know that relatively small releases (e.g., hundreds of gallons) can persist for years. Consequently, we can conclude that actions that leave hundreds of gallons of LNAPL in place are unlikely to restore a release area to background conditions in the near term. Beyond this the question of source longevity is challenging.

As a starting point one can define longevity of a release as the time required for concentrations of regulated compound to drop to a level where the site can be closed. Next one can apply a model. Most models that can address this topic are not user friendly. In an effort to address this limitation, API developed LNAST (LNAPL Dissolution and Transport Screening Tool) and the companion document *Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Concentration*, API Publication 4715, Huntley and Beckett (2002). Inherent to all models, including LNAST, are simplifying assumptions. Reflecting on the assumptions used in LNAST, it is most appropriately employed as a qualitative tool for screening options.

Specific analyses that can be conducted with LNAST include:

LNAPL Recovery − Given an initial condition, and a method of hydraulic recovery, the rate of LNAPL recovery is predicted (See Figure 8).

Groundwater Quality as a Function of Time at the Downgradient Edge of the Source − Given either an initial condition or the LNAPL remediation end point predicted in the LNAPL recovery tool, this predicts groundwater concentration at the downgradient edge of the source area (See Figure 9).

Dissolved Phase Concentrations − Given the source calculated using the LNAPL depletion option concentrations downgradient of the source can be calculated as a function of time (See Figure 10).

The LNAST model and associated documentation is available on API web site (www.api.org/lnapl). Overall this is a remarkable tool for gaining insight into how LNAPL depletion affects water quality.
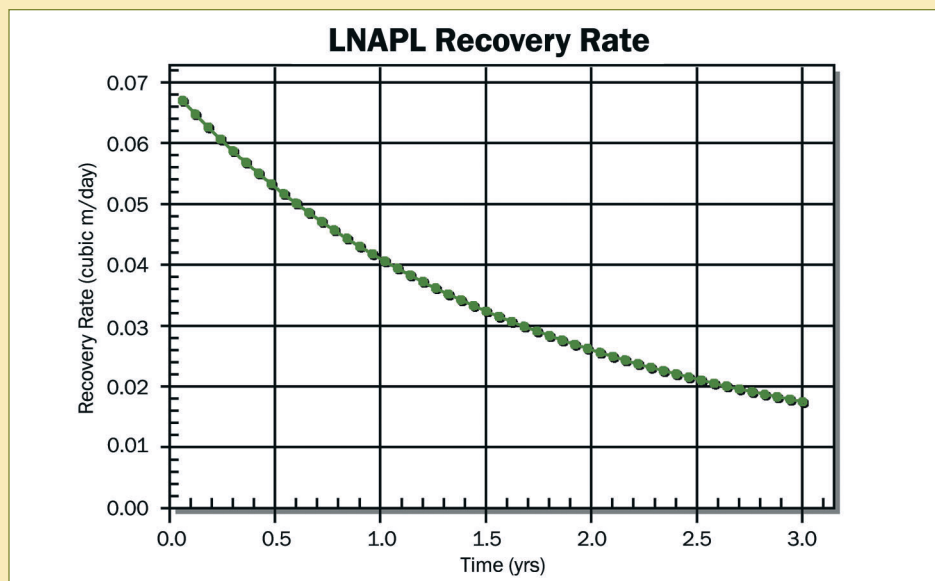

Figure 8 − LNAPL production predicted (using LNAST)

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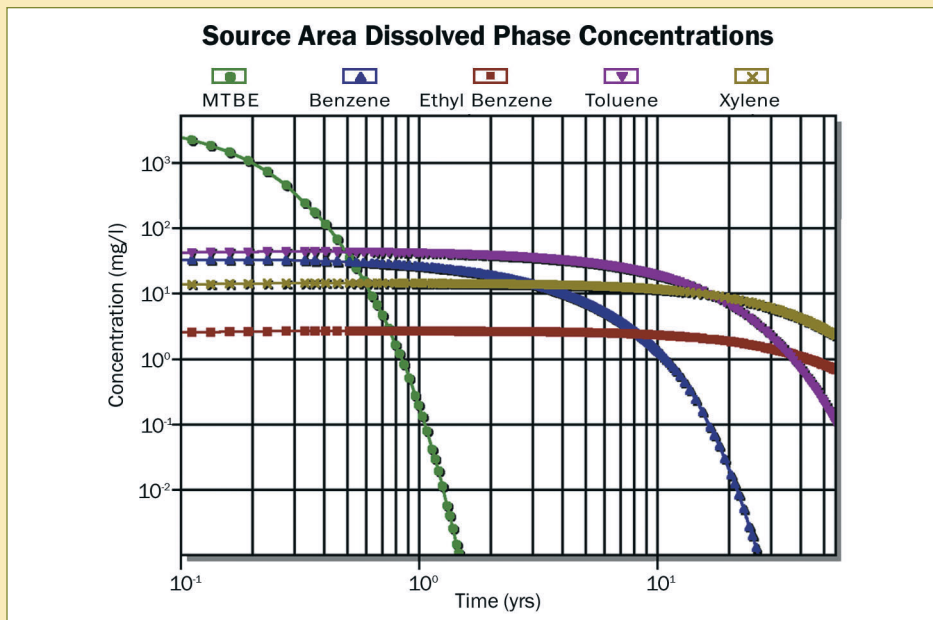
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Figure 9 – Water quality at the downgradient edge of an LNAPL release as a function of time after LNAPL depletion (using LNAST)
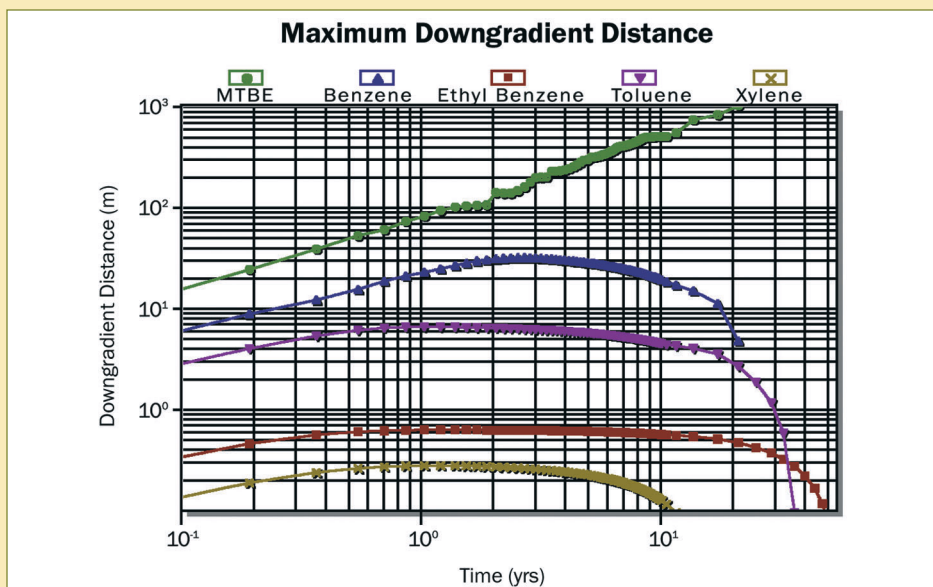

Figure 10 – Downgradient extent of water quality exceedances (prescribed concentration) after a given amount of LNAPL depletion (using LNAST)

WHAT ARE SOME EXAMPLES OF SITE CONDITIONS WHERE *IN SITU* LNAPL TREATMENT IS UNLIKELY TO IMPROVE GROUNDWATER QUALITY OR OTHERWISE REDUCE RISK? CONVERSELY, WHAT TYPES OF SITES ARE LIKELY TO BENEFIT FROM LNAPL TREATMENT?

Primary features that govern the potential to achieve meaningful improvements in groundwater quality are geology, the size of the site/release, and the degree of surface obstruction (e.g., buildings). In general, small sites (e.g., USTs), with no surface obstructions and relatively uniform conductive sediments will offer the best chance to achieve meaningful improvements in water quality via *in situ* treatment. However, this is not to say that small sites are necessarily easy. There are more than a few small sites that have not attained closure. On the other hand, at large sites with large surface obstructions (e.g., refineries) and intermixed high and low conductivity sediments, it is often implausible to achieve meaningful improvements in water quality via *in situ* treatment.

In more detail geologic factors include:

Fine-Grained Sediments − Fine-grained sediments are challenging in that LNAPL tends to be sparsely distributed along secondary features such as sand seams, root holes, consolidation joints, and burrows (See Figure 4, Panel 3). These features can be difficult to locate. Furthermore, these sparse features can be poorly connected and consequently, LNAPL recovery is difficult.

Complexity of the Subsurface − As intervals containing LNAPL become more complex (e.g., discontinuous inter-fingered layers of high and low conductivity) the ability to locate and sweep out LNAPL decreases. Furthermore, as has been seen with chlorinated solvents (Parker et al., 1997), high concentrations adjacent to LNAPL can drive dissolved phase LNAPL constituents into stagnant zones (e.g., clays) via diffusion. This process (matrix diffusion) depletes LNAPL and creates a long-term in situ source of dissolved phase contaminants. This latter concern can be a significant problem in fractured sedimentary rock, fractured clay such as saprolite, and with high solubility LNAPL constituents such as MTBE (methyl tert-butyl ether).

Other primary factors are anthropogenic and include:

Size of Site/Release − As groundwater passes through an LNAPL zone, LNAPL constituents dissolve. At larger sites/releases flow paths through the source will be longer. A consequence of this is that it will be necessary to remove a greater fraction of the LNAPL at a larger site, as compared to a smaller site, to achieve a similar near-term improvement in water quality.

Surface Obstructions − As the frequency and size of surface obstructions (e.g., buildings, roads, process units) increases, access for investigation and construction of recovery systems becomes constrained. As this occurs the potential for failure to identify and/or to poorly sweep LNAPL zones increases.

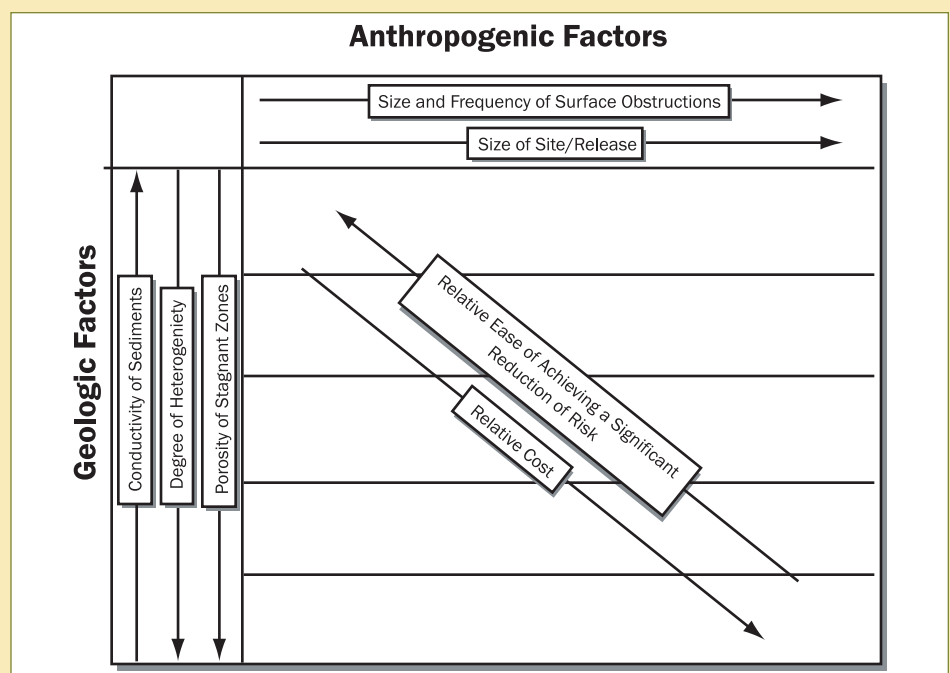The above general concepts are summarized in Figure 11.

Figure 11 − Factors governing 1) the potential to achieve a significant reduction in risk and 2) the cost of LNAPL depletion (arrows point in the direction of increase of the noted property)

WHAT CONDITIONS DRIVE THE NEED FOR *IN SITU* TREATMENT OF LNAPL RELEASES?

Building on work by Chuck Newell[6] and Tom Sale[7], Table 1 identifies common goals associated with LNAPL remediation and conditions that would be associated with more and less need for depletion of LNAPL using in situ techniques. At a conceptual level this provides insight into the need for *in situ* remedies as a function of site characteristics.

DESIRED BENEFIT	RELATIVE NEED		
	MORE NEED FOR *IN SITU* LNAPL DEPLETION		LESS NEED FOR *IN SITU* LNAPL DEPLETION
Reduced potential for LNAPL migration as a separate phase liquid	Known active migration of LNAPL (e.g., discharge to surface water)	Reduced potential for LNAPL migration as a separate phase liquid	Immobile residual LNAPL
Reduced source longevity	Large ongoing site care requirement cost Known impacts to receptors (e.g., surface water or wells) High probability of achieving near-term improvements in water quality		Low site care requirement Low resource value (e.g., natural exceedances of secondary standards) Low probability of achieving meaningful improvements in water quality
Near-term enhanced attenuation of a dissolved plume due to reduced loading from an LNAPL zone	An expanding dissolved phase plume	Stable dissolved phase plume	Shrinking dissolved phase plume
Near-term reductions in dissolved phase loading to receptors	Presence of known or soon-to-be impacted receptors	Potential future impact to receptors	No plausible impact to receptors
Near-term attainment of MCL	Need for rapid improvement in site conditions (e.g., impending property transfer)		Low risk with current and likely future land use

Table 1 – Factors affecting the need for *in situ* treatment of LNAPL releases

6) Chuck Newell, President, Groundwater Services, Inc.
7) Tom Sale, Assistant Professor, Colorado State University.

I'VE READ STUDIES ABOUT INNOVATIVE TECHNOLOGIES THAT REMOVE > 90% OF THE LNAPL IN A CONTAMINATED SOIL. HOW ARE THESE RESULTS IMPORTANT IN TERMS OF AN OVERALL PHILOSOPHY TOWARDS ADDRESSING LNAPL IMPACTED SITES?

Currently, a suite of technologies is generally considered to deplete LNAPL. These include pump and treat, dual phase liquid extraction, soil vapor extraction, bioventing, air sparging, and vacuum enhanced LNAPL recovery (bioslurp). All of these technologies have been recognized to have niches and limitations. In response to the limitations, new approaches for *in situ* depletion of LNAPL continue to evolve. Much of the scientific basis for these was developed by the petroleum production industry starting in the early 1950s. Today's list of innovative *in situ* technologies includes thermal (steam and electrical heating), surfactants, and chemical oxidants. Primary factors limiting these technologies are uncertain efficacy and high cost.

In more detail, at LNAPL sites it is common to be pressed by the limitations of proven technologies to consider innovative technologies. In doing so one should consider the following:

Cost versus Benefit − Many of today's innovative technologies have application costs on the order of $1 − 10 million/acre. Such costs can be inconsistent with the risk posed by a site and the value of the land. Furthermore, proven alternatives (e.g., excavation in select instances) may have lower costs and greater performance certainty.

Scaling and Performance − Common metrics for performance are the fraction of LNAPL recovered and near term improvements in water quality. The performance of most innovative technologies is typically based on small-scale field demonstrations conducted at promising locations. Moving to real sites with increased heterogeneity and greater size has the potential to reduce performance.

Adverse Impacts − Today's innovative technologies (thermal, surfactants, and chemical oxidants) are intensive. As such they hold the potential to effect adverse migration, risk to onsite worker, and risk through overall project life cycle activities (e.g., risk associated with transport of equipment, chemicals left in place, and air emissions from power generation). One should always consider whether the risk reduction attainable with innovative technologies is meaningful when compared to the risk of the remedy itself.

Altered Site Care Requirement − Considering results from models such as LNAST (Huntley and Becket, 2002) and field demonstrations (e.g., Simkin et al., 1999) it seems likely that essentially all of the released LNAPL will need to be recovered to effect a meaningful change in near-term site care requirements. Given this, a key factor limiting investment in innovative technology has been the prospect that they will do little to alter near-term site care requirements.

AFTER IMPLEMENTING THE BEST TECHNOLOGY, THERE WILL STILL BE RESIDUAL LNAPL IN THE GROUND AT MY SITE. HOW CAN I DETERMINE WHETHER VAPOR MIGRATION WILL BE A PROBLEM?

Volatile LNAPL compounds can partition from LNAPL and/or from groundwater to soil gas. Once in soil gas the compounds partition between the soil gas and soil water and migrate in soil gas via diffusion and advection. As in the groundwater zone, the extent of hydrocarbon vapor plumes is limited by natural *in situ* physical and biological processes (e.g., Johnson et al., 1998, Roggemans et al., 2001, and Johnson, 2002).

In general vapor migration should be a concern when either LNAPL or dissolved plumes (containing volatile compounds) exist at shallow depths under structures. Structures can include buildings and utility vaults. Vapor migration concerns can be addressed through monitoring, modeling, and/or physical controls such as positive pressures in structures. The optimal approach depends on site-specific conditions.

Currently, risk associated with vapor migration is an area of active research and debate. One focus area is reconciling the widely different standards of State and Federal programs. With this, a clearer basis for deciding when vapor migration needs to be actively addressed will develop. Until guidance has been reconciled best practice involves evaluating sites on a case-by-case basis and tracking the evolving state of knowledge.

THE WORK OF API AND OTHER RESEARCHERS SEEMS USEFUL WHEN APPLIED TO SITE-SPECIFIC PROBLEMS. HOW DOES IT AFFECT THE OVERALL PICTURE OF LNAPL MANAGEMENT?

Over the last thirty years universities, government, and industry have invested heavily in research associated with associated with LNAPL releases. Based on this our understanding of processes governing LNAPL releases have evolved dramatically. The reward has been the displacement of misconceptions by sound science. As an example, perceptions that LNAPL and associated groundwater and vapor plumes would migrate large distances from release points have been shown to be largely untrue (e.g., Rice et al., 1995 and Roggemans et al., 2001). Unfortunately, it has also been shown that *in situ* cleanup is not as simple as pumping out a tank. Complex physical processes and hydrologic conditions limit our ability to restore groundwater in LNAPL zones to

pre-release conditions (see Wiedemeier et al., 1999).

Given an evolution of knowledge, the paradigm for managing LNAPL releases has matured. Today we recognize the following:

◆ Our experience (now bolstered by readily available sound scientific theory and models such as such as LNAST, Huntley and Beckett, 2002) leads us to the realization that managing LNAPL may require strategies with long timeframes. As such we need to recognize the need for passive engineering controls, institutional controls, and appropriate land uses.

◆ Recognizing the practicalities of *in situ* remedies we need to focus our resources on those instances where tangible benefits can be achieved. Specifically we need to apply *in situ* source technologies in those areas where there are real problems (see Table 1) and where there is a high relative potential for success in reducing risk (Figure 11).

◆ While innovative technologies hold promise we need to consider their application within a holistic context. Care needs to taken to avoid solutions that pose more risk to human health and ecosystems than the problems we are trying to solve.

THERE SEEMS TO BE A LOT OF DIFFERENT REGULATIONS, GUIDELINES AND OPINIONS ABOUT "HOW CLEAN IS CLEAN" WHEN IT COMES TO LNAPL SITES. HOWEVER, THERE ARE TECHNICAL LIMITS TO TOTAL LNAPL REMOVAL. HOW DO WE RECONCILE THE POLICY AND TECHNICAL CONFLICTS AND MOVE FORWARD FROM HERE?

Regulation of LNAPL releases falls to a diverse set of state and federal programs. Through all of this a broad range of answers to the question "how clean is clean" has developed. The common thread of these programs is a desire to effectively manage

risks posed by historic LNAPL releases. The material described herein provides a basis for dialogue as to how this can best be accomplished. We encourage readers to consider the responses carefully and to apply the described tools. Through this,

parties can work together within the context of sound science and engineering to craft optimal solutions for the challenges posed by the unique attributes of individual sites.

SUMMARY

By necessity, sound solutions are founded on sound understanding. As such, the first step in addressing LNAPL releases is to recognize subsurface LNAPL as a multiphase flow problem. Historical analyses of LNAPL problems as single-phase flow problem (e.g., tank and pancake models) have led to flawed expectations and inefficient use of resources. Next the challenge of trying to clean up LNAPL to pre-release conditions is large. In particular, multiphase flow processes trap LNAPL, natural rates of depletion are slow, the subsurface is complex, and available technologies have limitations. With all of this it is not surprising that the best we can do often involves leaving a fraction of the released LNAPL in place.

In the face of less than perfect solutions dealing with LNAPL releases is a matter of managing risk. A good place to start is to evaluate the need for *in situ* remedies as a function of site characteristics (Table 1). This can help resolve the issue of what needs to be done. Next one can conceptually evaluate the potential for risk reduction and cost as a function of site conditions (Figure 11). This is useful in managing expectations. Inherent to Table 1 and Figure 11 is the observation that not all sites are the same. A consequence of this is that solutions need to be tailored to the characteristics of individual sites.

A first step in developing tailored solutions is to quantitatively address the questions of what needs to be done and what can be achieved. In recent years this process has been streamlined through the development of "user friendly" tools presented in Charbeneau et al. (1999), Charbeneau (2003), Sale (2001), Huntley and Beckett (2001), and Aqui-Ver, Inc. (in preparation). It is our hope that these tools and these responses to frequently asked questions will help facilitate use of sound science and engineering to craft optimal solutions for LNAPL releases.

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