



Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites

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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.

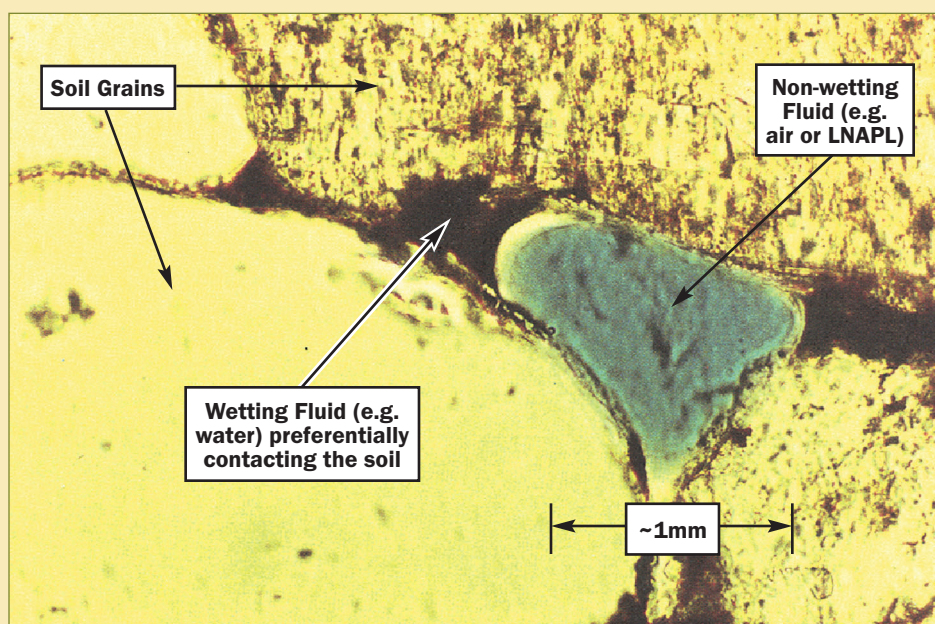


Figure 1 – Multiple fluids in the pore space of a granular porous media (From Wilson et al., 1990)

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.

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WHAT HAPPENS WHEN LNAPL IS RELEASED?

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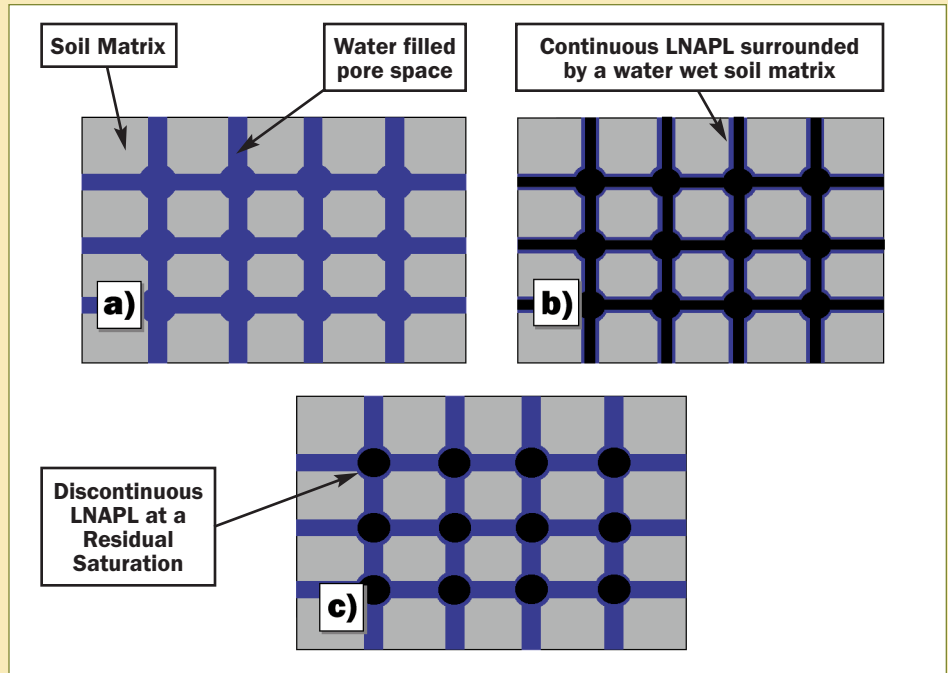


Figure 2 – Groundwater zone with continuous and discontinuous (residual) LNAPL occurrence in an idealized fracture network (After Wilson et al., 1990)

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 McWhorter¹, 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 Miller³ 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.

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.

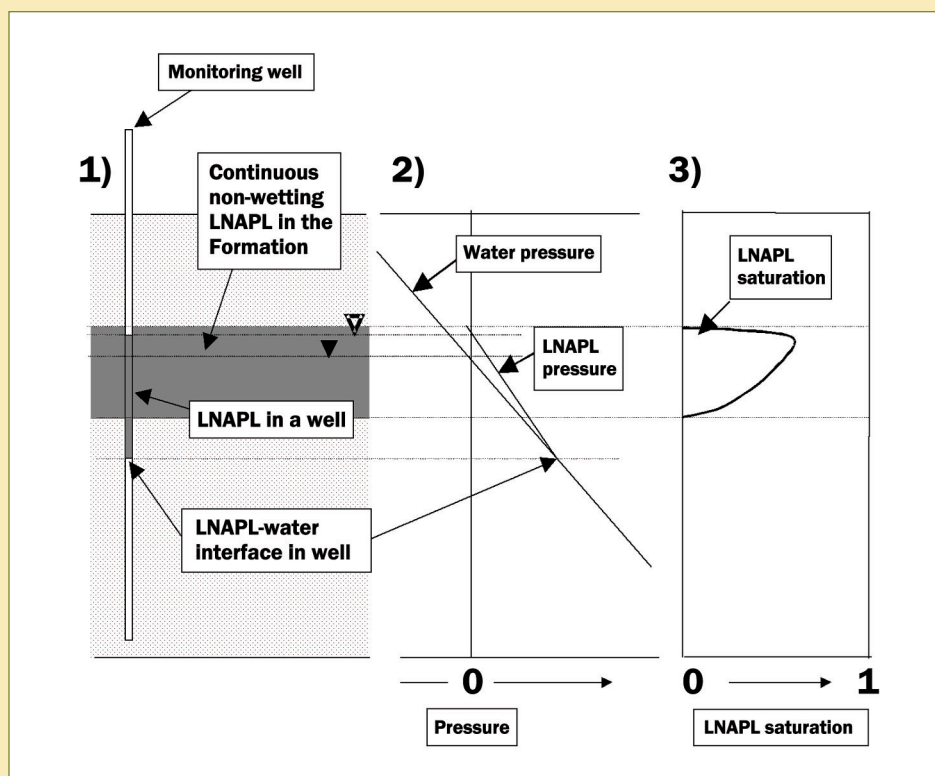


Figure 3 – Idealized conceptualization of LNAPL in a well and adjacent formation

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 ($\text{Pressure} = \text{Fluid Density} \times \text{Gravitational Coefficient} \times \text{Height}$). 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.

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