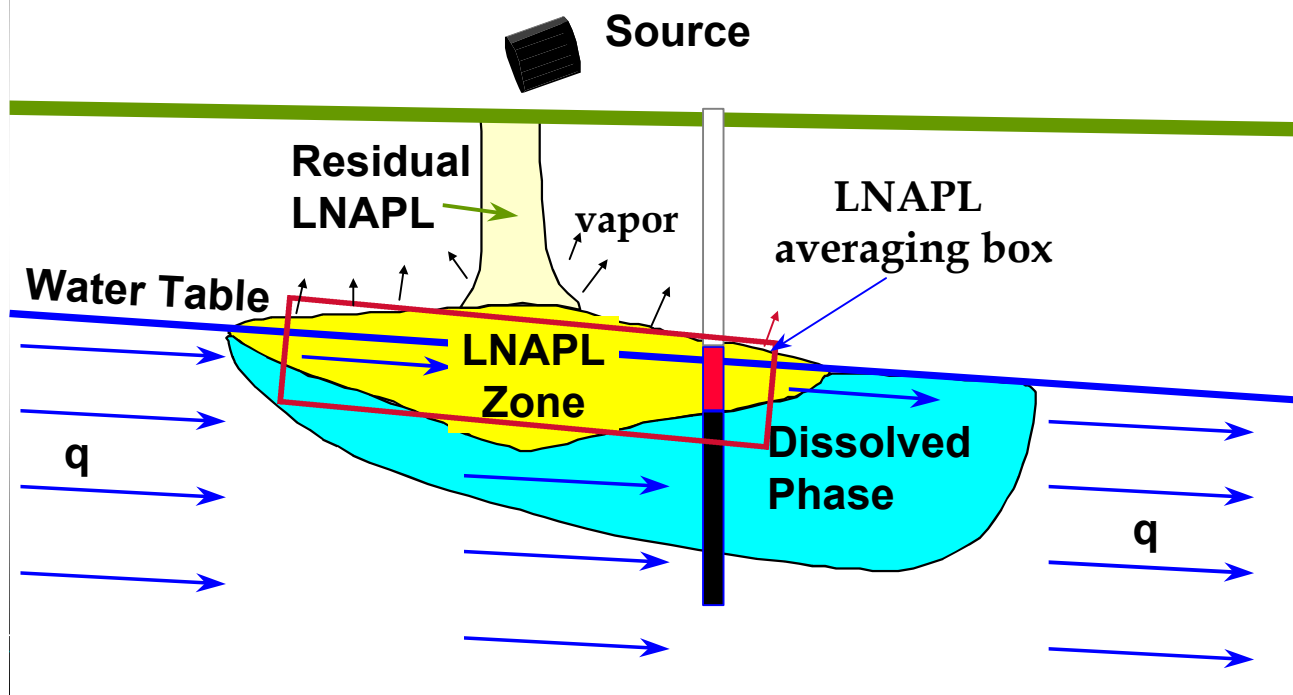


Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Magnitude

Regulatory Analysis and Scientific Affairs Department

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Conceptual Model



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FOREWORD

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EXECUTIVE SUMMARY

For many decades, the oil production industry has recognized that significant limitations exist to complete extraction of oil from geologic formations. Attempts to recover fuels and crude oil (collectively known as light nonaqueous phase liquids or LNAPL) accidentally released to the subsurface encounter similar limitations. This report explains how multiphase fluid mechanics (mixed presence of LNAPL, water, vapor) relate to these recovery limitations. The report further explains how the endpoints to recovery relate to both the longevity of the LNAPL as a source of dissolved-phase and vapor-phase constituents and to the downgradient dissolved-phase concentrations. This work is focused on LNAPLs, but the general principles also apply to many aspects of dense nonaqueous phase liquid (DNAPL) recovery and risk.

Release of an LNAPL to the subsurface introduces the potential of several risk factors to nearby receptors: (1) Vapor phase migration of volatile constituents from LNAPL in the vadose zone to the surface. (2) Dissolution of constituents from LNAPL in the vadose zone through infiltration of recharging waters, and subsequent downgradient movement of those constituents once those waters encounter the water table. (3) Release of sufficient LNAPL that it exceeds the capacity of the vadose zone to absorb it, resulting in the accumulation of a mobile LNAPL lens above and below the original groundwater table. (4) Upward vapor phase migration of volatile constituents from the above LNAPL lens to the land surface, and (5) Downgradient migration of dissolved-phase constituents resulting from dissolution of the LNAPL lens.

This report was prepared to synthesize the physical and chemical behavior of LNAPL in contact with groundwater, and to link those aspects to cleanup expectations. It does not deal with the mechanisms related to risk factors (1) and (2) above, which are processes limited to the vadose zone. The report deals with the zone between the top of the LNAPL capillary fringe and the lowermost observation of LNAPL in the aquifer. The report outlines the following:

1. The fundamental theory, with supporting field and laboratory observations, that controls the distribution and mobility of LNAPL and water between the top of the LNAPL capillary fringe and the lowermost occurrence of LNAPL in the aquifer.
2. The effect of remediation on the distribution and mobility of both the LNAPL and water within the zone of interest.
3. The dissolution of compounds from the LNAPL into groundwater flowing both through and below the LNAPL-impacted interval.
4. Volatilization of that LNAPL.

5. The effects of all of the above on the concentrations of soluble LNAPL constituents both within the source area and downgradient of the source area.

When LNAPL distribution and cleanup are linked to chemistry, the hydraulic recovery limitations can be placed in a risk-benefit context. The linked physical and chemical calculations show why, under many conditions, hydraulic recovery of LNAPL may have little or no benefit in reducing the magnitude or longevity of the risk downgradient from the LNAPL source area. The technical evaluations also show that chemical alteration of the LNAPL source may achieve compound specific cleanup goals that cannot be reached through hydraulic methods. For any remediation strategy, the short and long term benefits can be evaluated against the cost, time, and probability of achieving cleanup targets.

The fundamental principles described in this report have been organized into a software utility, called LNAST (LNAPL Dissolution and Transport Screening Tool). This software utility links the series of analytic solutions that predict LNAPL distribution, dissolution, volatilization, and downgradient dissolved-phase concentration through time, both with and without remediation through hydraulic means. Because the assessment described in this report has several linked aspects, or “tools”, for assessing LNAPL impacts, cleanup, and chemical transport, we will refer the combination of the underlying principles, the resulting mathematical solutions, and the software as a “toolkit”.

Because the solutions are analytic, they make many simplifying assumptions. Therefore, the linked suite of physical and chemical calculations will not provide a detailed representation of the site. The calculations described in this report, whether solved in a spreadsheet environment or using the software utility, are designed as screening tools only. The results of the calculations cannot be precisely calibrated to site conditions, just as the results of other screening models cannot. The toolkit described in this report is most properly considered as a quantitative conceptual model to be used for screening decision-making. There is a deliberate compromise between screening analytic methods versus numerical calculations that can consider a more complete range of complexities. While it is clear that conditions not considered by the software utility, such as complex vertical and lateral variations in soil properties, seasonally varying groundwater elevations, and laterally varying groundwater flow velocities near the LNAPL are important, the parameters necessary for such evaluations are not often available. Further, the effort involved in numerical multiphase, multidimensional modeling is significant. The approach presented here is therefore designed to use available information in the best manner possible, but it should be clear that uncertainty will exist in the results. The recommended use of the toolkit is expected to produce conservative results. If more accurate or detailed assessment is needed, numerical modeling and/or advanced data collection will be warranted, consistent with the higher-tiered levels of effort in many risk assessment guidelines (e.g., Risk-Based Corrective Action, ASTM 1995; Risk Assessment Guidance for Superfund, EPA, 1995). Therefore, while simple to use, this screening conceptual evaluation method requires good user judgment and awareness of the limitations.

The presence of multiple phases (water, LNAPL, vapor) in porous material influences the movement and transport of each phase under ambient or remediated conditions. Multiphase fluid mechanics and other principles are used to estimate the pore fluid fractions and their mobility under a variety of conditions. The distribution and composition of the LNAPL then determines the equilibrium chemical partitioning into groundwater and vapor. Ultimately, the application of these principles results in estimates of the time dependent concentration of soluble components partitioning out of the LNAPL and into groundwater, with a link to vapor flux under ambient flow and partitioning conditions. For instance, one could look at chemical partitioning from an LNAPL source that has had no remediation action, or one could consider the same source after some cleanup effort (but not during that effort). This toolkit does not directly consider institutional controls, such as plume containment, that are often an important component of risk management. However, one could use the toolkit to consider the time frame over which an institutional control might be appropriate.

Chemical concentration is the metric of this toolkit. All other things being equal, risk is proportional to the chemical concentration reaching receptors. Therefore, one can evaluate the risk/benefit of various LNAPL remediation strategies by looking at the concentration reduction associated with remediation. Specific site risk must be calculated separately by the user, as risk depends not only on the concentrations reaching the receptors, but also other factors in the exposure scenario, including the receptor characteristics, current and future land use, and other factors that are not part of this work.

In developing this multiphase approach, several observations and conclusions have been reached regarding the importance of LNAPL distribution, its chemical character, and source remediation. Several technical issues are isolated and summarized below.

The Effect of Soil Type

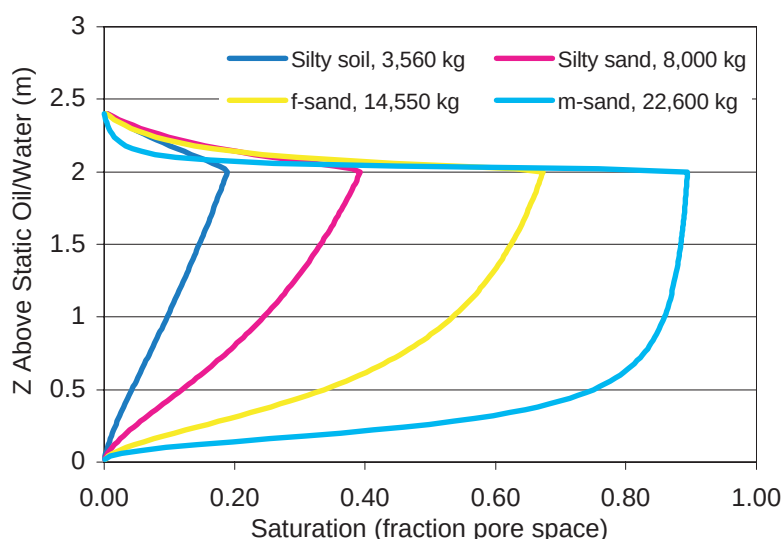


Figure E-1. Gasoline saturation curves for 2 m observed well thickness in several soils at vertical equilibrium. The total mass is for a 10 x 5 m areal extent.

For a given observed well thickness, LNAPL saturation and mass decreases strongly in the zone between the LNAPL/air and LNAPL/water interfaces in the well as the pore size gets smaller (Figure E-1). This, in turn, has a strong impact on the relative source longevity, which is also, dependent on the groundwater flow conditions. If one assumes the same net regional groundwater flow through all soils, then depletion is fastest in the fine-grained materials, because of less mass and greater relative water flow (Figure E-2a). If the same gradient is

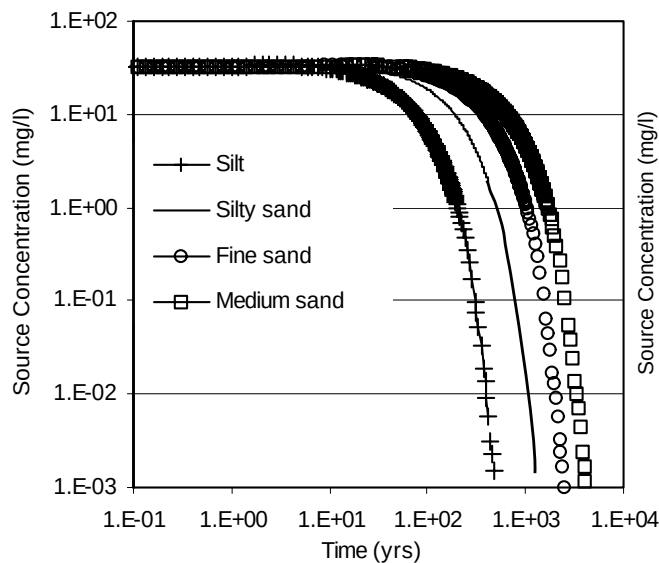


Figure E-2a. Source depletion of benzene from gasoline where the regional flow is the same for each soil (no biodecay in the source zone).

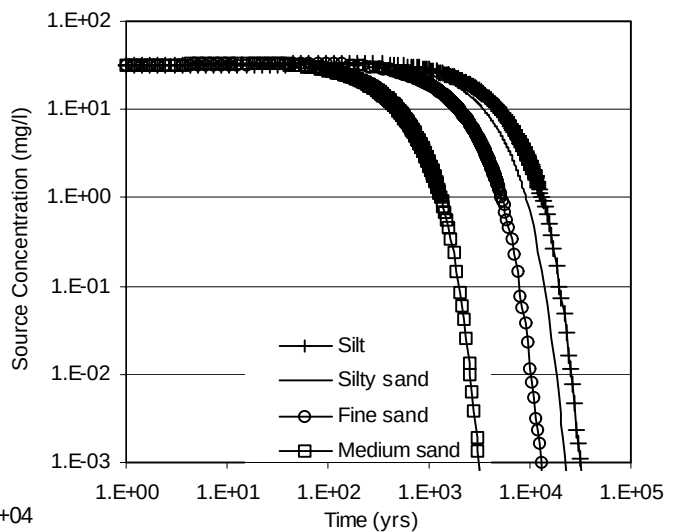


Figure E-2b. Source depletion of benzene from gasoline where the hydraulic gradient is the same for each soil (no biodecay in the source zone).

assumed for all soils, then the flow through the finer-grained units is small and the source depletion time is long (Figure E-2b). Therefore, the soil type exerts a strong influence on source residence time with or without cleanup. These estimates do not include volatilization from the LNAPL, which will be discussed below.

Effect of LNAPL Thickness

The mass distribution of LNAPL and the related source longevity for any compound of interest are exponentially related to soil and fluid capillary properties, and to capillary pressure, which can, in turn, be related to the LNAPL thickness observed in a monitoring well at vertical equilibrium (VEQ). For a range of thicknesses from 0.25 to 2.0 meters in a fine-sand, the volume varies over nearly two orders of magnitude (Figure E-3). This has a very large impact on the chemical component depletion from the LNAPL under natural groundwater flow conditions (Figure E-4).

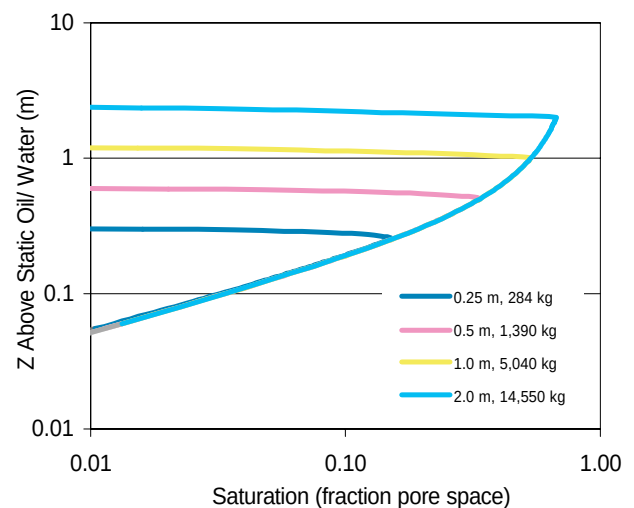


Figure E-3. Equilibrium gasoline profiles at various well thicknesses, plotted log-log to expand scale.

Effect of LNAPL Residual Saturation

LNAPL residual saturation is the smallest saturation remaining in the formation against applied hydraulic recovery and is the theoretical endpoint of LNAPL hydraulic recovery. It is also a highly optimistic endpoint because real hydraulic variability, well efficiency, well interference, aquifer heterogeneity and other factors all combine to diminish actual recovery and leave more LNAPL in the formation. For instance, for an initial

gasoline thickness of 1 m, we find that the benefit of LNAPL removal decreases and the source benzene concentration residence time approaches that of a non-remediated condition as the residual gasoline saturation increases from 5 to 30% for a sand soil (Figure E-5). Since one cannot hydraulically reduce LNAPL saturations below residual saturation, this factor is very important for any site where hydraulic recovery may be considered of potential benefit.

Contrast in Components of Concern

The effective solubility and mole fractions of the various compounds in fuels have a significant effect on the longevity of the compounds within the source. For example, we have compared MTBE and benzene in gasoline with naphthalene in a diesel for 2 m of observed thickness in a fine-sand (Figure E-6). Because the effective solubility of MTBE and benzene are high relative to naphthalene, the source longevity between the components is separated by several orders of magnitude, with naphthalene present for tens of thousands of years for the conditions considered (Figure E-7).

Component Volatilization

Volatilization is another potential mass loss mechanism from the LNAPL source depending on fuel volatility and site subsurface conditions. Using the example above, we have looked at free volatilization from the source. MTBE and benzene both have substantially higher vapor pressures than naphthalene. Comparison of Figure E-7 (source depletion without volatilization) to Figure E-8 (depletion with volatilization) demonstrates that inclusion of volatilization as a mechanism of source depletion causes a reduction in the potential source longevity of MTBE and benzene, but naphthalene longevity remains essentially unchanged. Be aware that free volatilization from the LNAPL source in the water table zone is rare. There are almost always impeding horizons such as surface covers and geologic conditions to be considered.

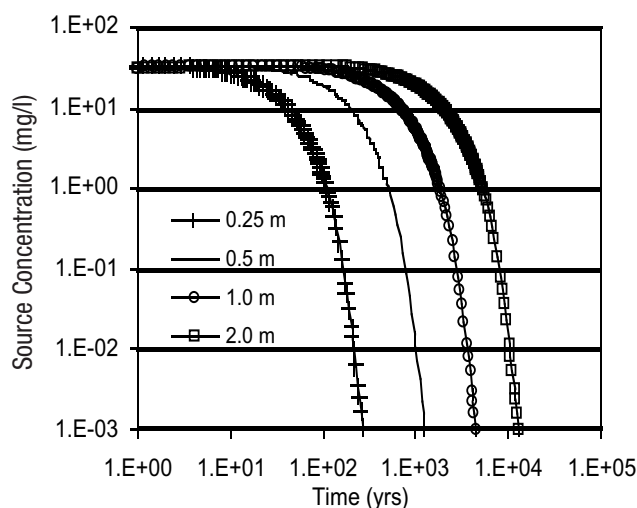


Figure E-4. Depletion curves for benzene associated with the vertically equilibrated (VEQ) profiles from 0.25 to 2.0 m.

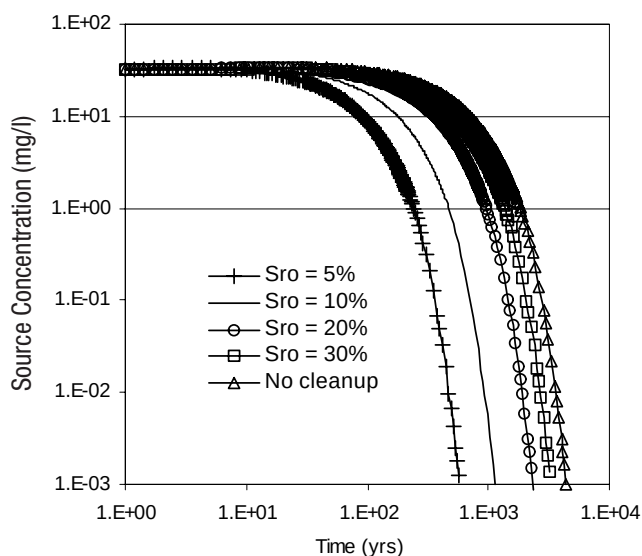


Figure E-5. Benzene source depletion calculation for various gasoline specific retention values in a fine-sand. The actual value for many sands in this class would be 15 to 30%.

This is not to say that component losses in the vadose zone are not significant as the LNAPL spill migrates downward to the water table region, particularly for volatile compounds like MTBE.

Remediation as a Function of Soil Type

There is a large contrast in the potential gains of hydraulic free product removal between coarse- and fine-grained soils, all other things being equal. Although fine-grained soils have lower LNAPL masses for the same observed LNAPL thickness condition, this lower saturation condition also significantly limits hydraulic recovery compared to coarser-grained soils. The same may be said for the air-phase if considering remediation by vacuum-enhanced methods. A comparison between source longevity for hydraulically remediated and non-remediated conditions in a finer-grained soil shows remediation impacts source longevity only slightly (Figure E-9). In contrast, for the same initial condition of 2 m of gasoline, remediation of coarser soils results in a more significant decrease in source longevity.

Effect of Regional Groundwater Flow Rate

The regional groundwater flow rate controls the source depletion rate in the absence of volatilization because it is responsible for the mass partitioning from the LNAPL. Therefore, one observes more rapid source depletion and more rapid decreases in the downgradient extent of a dissolved-phase plume more quickly in cases of high flow for the same

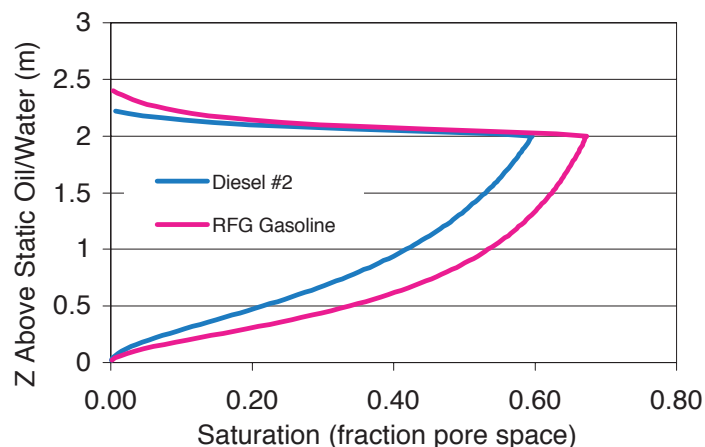


Figure E-6. Saturation profiles for 2 m observed fuel thickness, gasoline and diesel, in a fine-sand.

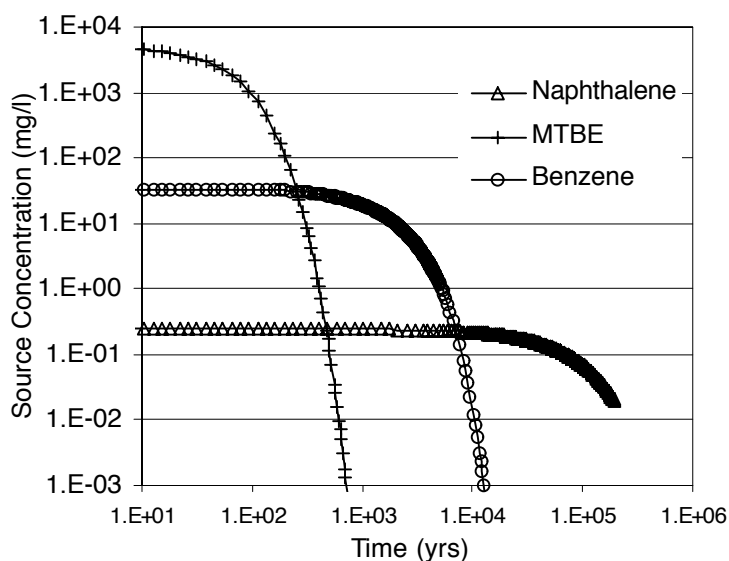


Figure E-7. Comparison of different fuel components and their longevity in the source under ambient conditions.

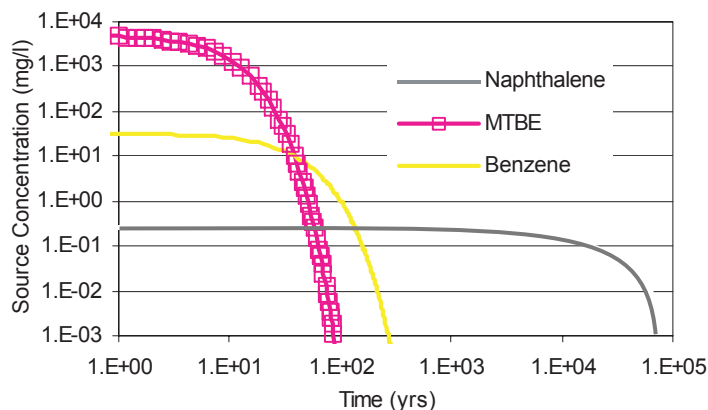


Figure E-8. The estimated source depletion graph for MTBE, benzene, and naphthalene allowing free volatilization from the source.

initial LNAPL mass distribution. The regional groundwater flow rate also impacts the potential downgradient extent of a given constituent concentration in a dissolved hydrocarbon plume, as does the specified biodecay rate.

Because the mass of LNAPL is very large compared to the solubility of its constituents, the longevity of the source is typically large compared to the time it takes for a dissolved phase plume to reach field equilibrium as a function of dissolution, transport, and the rate of biodegradation. Therefore, the downgradient extent of a given constituent concentration in a dissolved plume is almost entirely independent of the LNAPL source area conditions (Figure E-10). Possible exceptions are highly soluble compounds or very small LNAPL mass distributions in the source area.

It should be noted that dissolved-phase plume studies show that the extent of a stable, dissolved phase plume undergoing biodegradation, is not strongly dependent on groundwater flow velocity. This is likely due to the fact that biodegradation is often limited by the mass flux of oxygen and other electron receptors to the zone of biodegradation, which in turn is affected by groundwater flow velocity. This suggests that one might estimate higher biodecay rates in high flow settings, with a resultant diminishment in the diminishment in the downgradient extent of the plume.

KEY POINTS

From the points above and those developed in the body of this report, several summary observations and conclusions can be drawn. These observations and conclusions are derived from theory supported by lab and field data from the environmental field and many decades of petroleum production experience. The term “risk magnitude” is used as a relative indicator of risk potential based on the expected concentration of

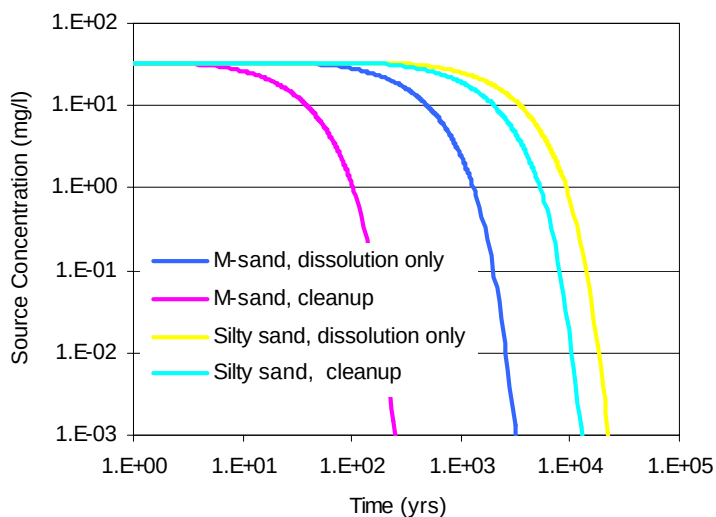


Figure E-9. Comparison of hydraulic LNAPL recovery cleanup versus initial conditions for a silty sand and a medium sand.

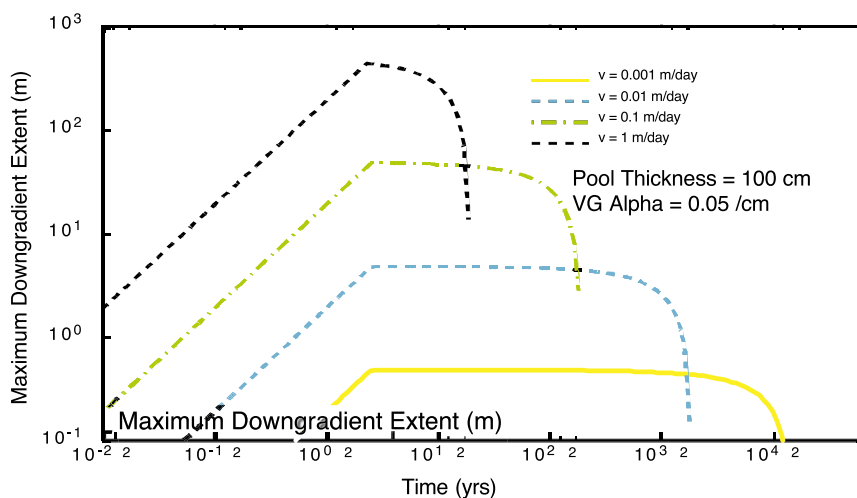


Figure E-10. The effect of groundwater velocity on the downgradient extent of benzene at a uniform decay rate.

a compound in groundwater or in the LNAPL phase. Whether or not a “risk” exists depends not only on concentration, but also on the nature of the potential receptors. Risk “longevity” refers to the time frame over which the risk magnitude remains relatively static.

1) For the groundwater and vapor exposure pathways, risk magnitude is strongly dependent on the chemical characteristics of the LNAPL source and the nature of potential receptors, whereas the risk longevity is strongly dependent on the mass distribution in the formation. The mass distribution depends strongly on soil properties and the characteristics of the LNAPL release. The zones of greatest LNAPL saturation within the source zone usually control the risk magnitude and longevity of groundwater and vapor impacts.

2) Under most conditions, hydraulic removal of LNAPL does not reduce the magnitude of risk in groundwater or vapor exposure scenarios, although there is a risk longevity reduction when mass is recovered. In permeable soils and under best-case conditions, the risk longevity reduction may be about an order of magnitude, or possibly a little more in rare cases. In lower permeability soils, risk longevity may be reduced only a few percent.

3) Hydraulic LNAPL recovery is not generally effective at mitigating existing groundwater risks unless both LNAPL and groundwater containment are successfully achieved. Hydraulic recovery has virtually no risk benefit in most cases with respect to the vapor phase exposure pathway. Under most conditions, free product containment intervention for the free phase must occur near the time of the release before excessive spreading and mobility reduction has occurred. Recovery and containment of dissolved-phase plumes are viable risk management options to mitigate groundwater receptor pathways, but will do little to treat the LNAPL source zone.

4) Any process that decreases the LNAPL saturation will decrease its mobility and recoverability. This means that LNAPL plumes become less mobile and recoverable through time as spreading results in smaller saturations. The pool becomes immobile when the LNAPL gradient is less than the capillary forces resisting further water displacement. This also means that LNAPL remediation is a self-limiting process since reducing saturations reduces the potential for further recovery.

5) In situ removal of specific chemicals of concern in LNAPL, using approaches such as vapor extraction, heating, or other enhancements, when feasible, reduces the risk magnitude of the release in approximate proportion to the corresponding mole fraction reduction in the source. The effectiveness of most cleanup technologies, however, depends on the ability to thoroughly contact the LNAPL with the remediation stream throughout the source area. Therefore, understanding of the LNAPL source characteristics and distribution is meaningful to any risk reduction strategy.

6) There is a widely held belief that the measured LNAPL thickness in a monitoring well exaggerates the thickness of LNAPL present in the formation adjacent to the well. However, fluid physics theory indicates that, at vertical equilibrium, the thickness of the LNAPL-affected interval in the aquifer will be greater than the LNAPL thickness observed in the well. In a few instances in the field, however, there may be situations where the LNAPL thickness appears greater in the well than the LNAPL-affected formation outside of the well. Heterogeneity and conditions where vertical equilibrium does not exist may produce this apparent thickness exaggeration.

From a corrective action perspective, it is important to recognize that the thickness of LNAPL in a well may exaggerate the *volume* of in-place and recoverable LNAPL in the formation. LNAPL exists at a variety of saturations in the formation over the vertical interval suggested by the thickness of the LNAPL in the well. However, substantial amounts of the LNAPL outside of the well will occur at low saturations that renders it immobile within the formation and unrecoverable.

7) For most conditions, observable plume thickness in observation wells and risk are unrelated, particularly under small observable LNAPL accumulations. However, large accumulations of LNAPL that return quickly to a well after bailing can imply local area mobility of the free phase product. Transport of the free phase LNAPL can often have undesirable outcomes and present a significant risk.

8) For the same capillary pressure conditions, LNAPL saturations are substantially smaller in fine-grained soils than in coarse-grained soils, all other things being equal. This effect combines with the low intrinsic permeability of fine-grained soils to produce very low mobility and potential recoverability in fine-grained materials. When the regional groundwater flow and volatilization from the fine-grained materials is small, the lifespan of LNAPL in these materials can be long.

9) LNAPL viscosity varies significantly for various petroleum products and crude oils and is inversely proportional to the effective LNAPL conductivity. Thus, for the same soil and product saturation, a fuel oil pool may be up to 50 times less mobile and recoverable than a similar pool of gasoline.

10) Industry and regulatory experience indicate that it is rare for hydraulic LNAPL removal schemes to recover more than 30% of the oil in place, although exceptional instances may yield 50-60%. When groundwater is produced, the ratio of product to water is usually less than 0.01 and typically decreases further with time.

11) For biodegradable constituents, the downgradient extent of the dissolved-phase plume is largely unrelated to the LNAPL mass distribution, unless the mass is very small. The maximum extent of the dissolved-phase plume is controlled by the groundwater velocity and degradation rates, which may be

related. Typical biodegradable plumes are expected to become stable in less than a few years.

12) The expected groundwater residence time of some compounds from LNAPL sources is on the order of decades to thousands of years. The residence time increases for larger pools with high LNAPL saturation and as the component solubility and its mole fraction in the source becomes smaller. Therefore, low volatility and solubility fuel components such as polynuclear aromatic hydrocarbons may persist at low concentrations for very long times. However, these same chemical attributes, coupled with bioattenuation and other factors, often buffer the risk magnitude of plumes from the long-lived sources.

13) From a technical standpoint, risk in a given exposure scenario depends on the points of compliance selected. If plumes are long-lived but also attenuated at some distance, there is obvious potential risk from direct contact within a certain radius of the plume, but no risk outside that zone. Therefore, the public, responsible parties, and regulators may benefit from a technical consensus on how to define and maintain compliance zones.

Section 1.0
ABSTRACT

Light nonaqueous phase liquids (LNAPL; *a.k.a.* petroleum fuels, “product” and crude oil) are common sources of hydrocarbons in both water and vapor phases, with all phases presenting potential health, resource, and environmental risks. Ample environmental and oil reservoir data have shown that complete recovery of oil from geologic formations is not generally feasible. Even at residual saturation (trapped and immobile), the LNAPL phase has a mass that is typically several orders of magnitude greater than normally present in sorbed, water, or vapor states, implying the potential for long-term impacts.

Regulatory agencies usually require a responsible party to “remove free product to the maximum extent practicable.” Lacking in ways to easily assess the mobility and long-term risks of LNAPL pools from site to site, arbitrary maximum LNAPL thickness in wells (e.g., 0.1 feet) is often adopted as endpoints for free product recovery. However, observed LNAPL thickness in wells has little or no relationship to the magnitude of risk presented before or after cleanup attempts. Often, free product recovery efforts are undertaken with little understanding of how much product can be recovered, how long the recovery will take and whether the site conditions will change significantly after the recoverable product is removed. This report is intended, in part, to assist in evaluating these issues.

This study provides quantitative theory and tools to evaluate LNAPL sources, their chemistry, and the effects various remediation strategies may have on groundwater and vapor exposure pathways. These exposure pathways are often a critical component of quantitative risk assessment. The study was designed to link the multiphase and chemical processes controlling *in situ* LNAPL distribution, mobility, and cleanup to quantify estimates of the time dependent concentrations within and downgradient of the LNAPL source. This work considers active flow of groundwater through the LNAPL impacted interval, which has generally not been considered in other analytic evaluations.

The results of this work suggest that the physical limitations to hydraulic free-phase recovery using current technology are such that significant health or resource risk reduction is gained only within a narrow range of chemical and geologic conditions. The greatest risk reductions, as measured by concentration reduction along an exposure pathway, occur in highly permeable soils and for volatile and soluble fuel components. The least effective risk reductions occur in low permeability materials and for fuels that have small volatility and solubility. Under many conditions, it is likely that LNAPL-sourced dissolved and vapor plumes will be present for decades to centuries unless treatment options improve significantly. The evaluation methods presented here can be used to show that the field endpoint, both chemical and physical, of any given cleanup method controls the long-term residual risk.

Section 2.0

INTRODUCTION

This report provides a series of linked analytic methods (or tools) to evaluate light non-aqueous phase liquids (LNAPLs) and their impacts in the water table region. The LNAPL conditions may be conceptualized under a range of conditions, including application of simplified cleanup strategies, under equilibrium conditions, and under user-defined conditions. The purpose is to assist in building conceptual site models that account for key processes and properties affecting the longevity and magnitude of chemical impacts associated with LNAPL spills in the water table region. As human and ecological risks are in part dependent on the chemical concentrations reaching receptors and the timing of those impacts, this technical methodology can assist in risk-based comparisons of various site LNAPL scenarios, including remediation endpoints. The metric of this evaluation method is concentrations in groundwater as a function of the LNAPL source conditions through time, with or without volatilization. There are no explicit risk calculations, as those are site and receptor dependent.

The report is focused on multicomponent petroleum products, although many of the principles apply to other NAPLs, including dense non-aqueous phase liquids (DNAPLs). Throughout the report, the term LNAPL will be used to describe petroleum fuels, crude oil, and other water immiscible compounds having a density less than water.

The impetus for developing this methodology has been decades of petroleum recovery experience coupled with more recent environmental experience that clearly demonstrates significant limits exist to complete LNAPL recovery from geologic materials. This suggests it would be useful to consider the various factors controlling LNAPL distribution and recovery and link those to the associated differences in the magnitude, longevity, and distribution of groundwater impacts. Obviously, LNAPL mass reduction seems inherently good, but the question is how to technically define “good.” If, for instance, a risk to groundwater is presented by a fuel release and we find that our common recovery technologies do not mitigate that risk, we would probably all agree that this is not “good.” Conversely, if mass removal reduces fuel mobility and risk longevity in a meaningful way, we would also probably agree that this is “good.” The intent of this toolkit is to help the user to distinguish, in a site specific context, between effective and ineffective remediation using concentration reduction as a consistent benchmark.

The building of this LNAPL screening method depends on several related attributes of LNAPL spills affecting the water table region. First, the multiphase hydrogeologic aspects of LNAPL in the water table region is considered for a range of possible initial conditions. Second, the partitioning and transport of chemicals from the LNAPL in groundwater is linked to the mass distribution and chemical composition of the LNAPL. Volatilization of compounds from the LNAPL may also be

considered. Because the screening evaluation method is based on several linked methods or “tools,” the term “toolkit” will be used throughout this report to refer to one or more of the various technical aspects. The “toolkit” is also organized in a software utility called API-LNAST (**L**NAPL **D**issolution **a**nd **T**ransport **S**creening **T**ool), which will be discussed subsequently. The LNAST program is primarily an organizational tool to aid the user in performing the linked dissolution, volatilization, and solute transport calculations. Use of the program is not necessary, as all the pertinent information, equations, and methodologies are also provided in this report.

The remainder of this introduction will develop an overview of concepts important to the LNAPL problem in the groundwater system, touch briefly on risk concepts, and discuss what this methodology considers. Following this overview, the report will discuss geologic, fluid, and chemical parameters important in the underlying description of the problem. Remediation aspects will also be developed to assist in bracketing the possible LNAPL conditions as a function of the cleanup strategy applied. Following this background and description of the important controls and parameters, a User’s Guide is developed for the included software utility API-LNAST. Example problems are also provided to assist in showing how evaluations might proceed.

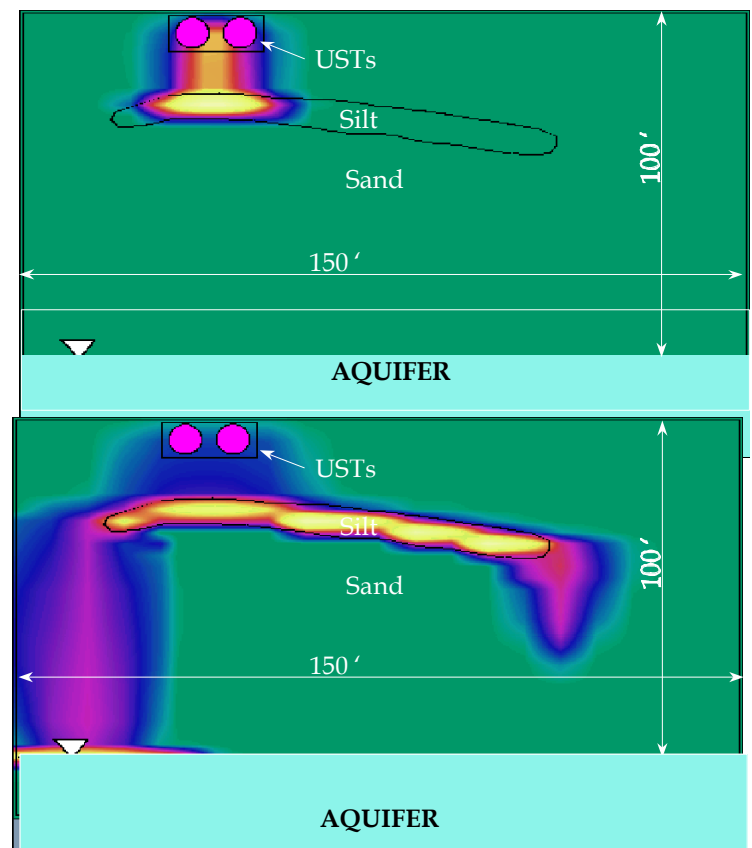
Throughout this manual, the active use of equations will be minimized and graphical examples will be used instead wherever possible to keep the focus on the principles, with some simple equations presented for elucidation of key ideas and concepts. Comprehensive development of necessary equations is provided in Appendices A and B. Appendix C provides a synopsis of parameter ranges for the various inputs needed for the calculations. Appendix D provides a brief overview of field “reality” checks that might be of assistance when considering the best application of the toolkit and the appropriate input parameters. Appendix E shows example input and output files.

2.1 LNAPL SPILL CONTEXT AND METHOD OVERVIEW

The body of field observations, supported by multi-phase fluid and chemical partitioning theory, indicates that the release of a fuel hydrocarbon will undergo the following evolution:

1. An LNAPL release begins with vertical drainage of LNAPL under gravity and capillary gradients (Figure 2-1a). The drainage is strongly influenced by soil characteristics and occurs most rapidly in dry, high permeability soils, and more slowly in wet or low permeability soils. As the LNAPL moves downward through the vadose zone it will be subject to physical and chemical process that include volatilization, entrapment of part or all of the LNAPL as residual phase (immobile), and dissolution of LNAPL components into soil pore water.

2. If the release is sufficiently large to exceed the residual retention capacity of the vadose zone soils, the LNAPL will eventually encounter the capillary fringe above the water table (Figure 2-1b); this also occurs for perched water table zones. As LNAPL encounters pore spaces completely or partially saturated with water near the water table, the weight of the LNAPL causes it to displace pore water until hydraulic equilibrium is achieved. At the same time, the large vertical gradient through the vadose zone dissipates into a lateral gradient in the capillary and water table zones. The lateral gradient is often semi-radial because of mounding of free product due to the resistance of the water wet materials to freely transmit the oil. The result is a free product mound, with a gradient that often has little relationship to the groundwater gradient.



Figures 2-1a & b. Multiphase calculation showing downward LNAPL spill propagation in cross-section at 2 weeks and 1 year. Notice deflection of oil by the silt bed & later-time mounding in the water table region.

3. Once the release of free product stops, the LNAPL in the water table region will eventually cease to move as the resistive forces in the water wet sediments balance the driving forces in the LNAPL pool. An absolute endpoint of this movement is when the LNAPL reaches field residual saturation, a condition where the effective hydraulic conductivity of the LNAPL is zero. This leaves a mass, often large, of LNAPL for secondary dissolved and vapor-phase transport (Figure 2-2). When immobile, the LNAPL presents a risk only as a source of dissolved-phase and vapor-phase compounds to the environment. It is important to understand that in the interval below the top of the oil capillary fringe, LNAPL and water *coexist* in a zone often characterized by observed free product in a monitoring well (the theory will be discussed subsequently). In this zone, both water and product “fight” for space, and interact chemically as well (Figure 2-2).

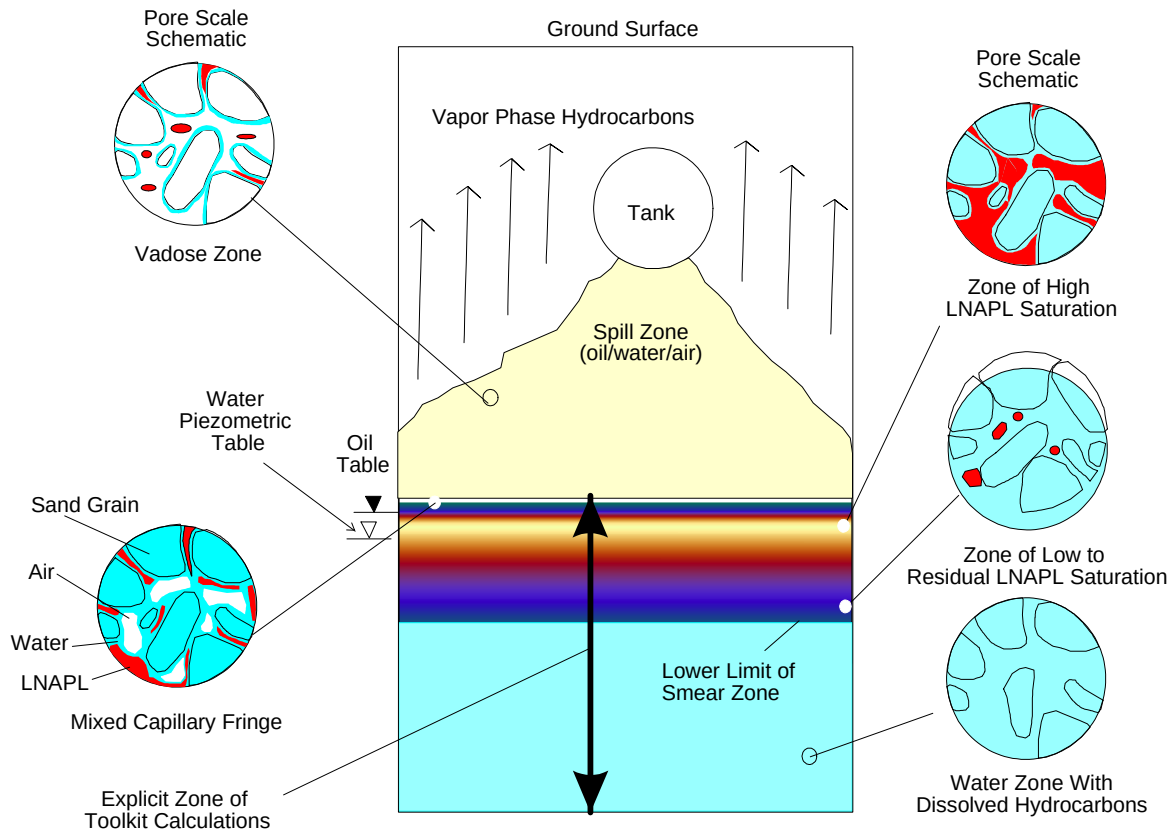


Figure 2-2. Schematic of an LNAPL spill showing different zones of impact from the source, in this case an underground storage tank (modified after White et al., 1996).

4. During the evolution of the LNAPL lens, external hydraulic factors may act to re-distribute all or portions of it. For example, water table fluctuations will tend to smear LNAPL vertically throughout the range of hydraulic variation, and often below the normally observed oil/water interface in a monitoring well.
5. As soon as the LNAPL encounters groundwater at or below the top of the groundwater capillary fringe, dissolution of soluble components of the LNAPL by groundwater moving below and through the LNAPL impacted interval begins. Thus a dissolved-phase plume starts to develop and, with time, grows in the downgradient direction.
6. For biodegradable constituents, the dissolved phase groundwater plume continues to grow until equilibrium is established between the rate of dissolution of the soluble LNAPL constituents and the rate of biodegradation. At this point, the plume stabilizes spatially. For non-biodegradable constituents, the dissolved-phase plume continues to expand until equilibrium is reached between the rate of dissolution from the LNAPL source area and the rate of dispersion (spreading) and dilution.

7. As dissolution and volatilization of soluble and volatile LNAPL compounds continues, the LNAPL becomes increasingly depleted of these compounds, resulting in decreasing concentrations of these constituents in the source area and a resulting contraction of the dissolved phase plume. This continues until the LNAPL is completely depleted of a constituent, and the dissolved-phase plume for the constituent disappears.

Overall chemical transport pathways (i.e., risk factors) potentially associated with this process include: (1) Volatilization of compounds from LNAPL in the vadose zone and upward migration of the resulting vapors to the surface; (2) Impacts to groundwater from dissolution of soluble compounds in LNAPL in the vadose zone (leachate); (3) Lateral movement of LNAPL in the water table region; (4) Volatilization of compounds from the LNAPL lens in the water table region and upward migration of the resulting vapors; (5) Dissolution and transport of soluble LNAPL constituents by groundwater moving through and below the LNAPL; (6) Potential volatilization and upward migration of vapors directly from the dissolved-phase groundwater plume. Remediation is designed to mitigate one or more of the risk factors above. When LNAPL is present, most remediation strategies target LNAPL mass reduction or changing the LNAPL chemistry such concentrations in the dissolved and/or vapor phase are reduced. Risk management and institutional control strategies may elect to address transport pathways without attempting to mitigate LNAPL impacts directly.

This technical methodology explicitly addresses items 4 and 5 above, with combined consideration of simplified aspects of remediation. Site specific parameters (estimated or measured) may be used to: (1) Evaluate the potential for LNAPL mobility; (2) Estimate the longevity and strength of the dissolving LNAPL source under conditions ranging from ambient conditions to those after some period of remediation; and (3) Simulate the behavior of the associated dissolved plume over time and distance downgradient of the source, in response to the selected degree of source removal. The method may be viewed as a site conceptual model that is mathematically based. As mentioned, the focus of the toolkit methods will be primarily on chemical concentrations in groundwater as a function of various LNAPL source and chemical conditions. However, the toolkit can also be used to evaluate simple mass reduction strategies, which could be a goal independent of groundwater concentrations or risk.

Human and ecological risks are in part dependent on the concentration reaching receptors; therefore one goal of this technical methodology is to assist in risk-based comparisons of various site cleanup options. The reader is reminded that the purpose of this work is not risk quantification, as that is strongly site and receptor dependent. The purpose is to provide links between LNAPL source conditions and resultant concentrations in groundwater under a range of scenarios that can be compared with independently estimated cleanup targets, risk-based or otherwise. If a specified condition fails to meet chemical target levels within a zone of compliance or time, then one would typically look at alternative strategies.

The technical method developed in this report allows the user to specify LNAPL conditions (e.g., saturation and spatial distribution) in the water table region for any combination of homogeneous soil and fluid properties. The LNAPL conditions in the water table region may then be acted upon by remediation, or left under the user specified ambient conditions. The toolkit also allows user prescribed conditions for simple layered systems without explicit hydraulic recovery estimates. Whichever path is taken by the user results in an estimated distribution of oil in the formation. That distribution then controls the dissolution of hydrocarbons out of the LNAPL into the groundwater and vapor phases. The user can specify the chemical compounds of interest within the LNAPL, and the time dependent concentrations of those compounds are calculated based on the initial mass and the progressive depletion of mass from the LNAPL source zone. Biodegradation of the LNAPL source is not considered, but biodegradation is allowed to act on the dissolved-phase plume, as specified by the user.

The vertical interval considered in the calculations is from the top of the oil capillary fringe to the lowermost occurrence of LNAPL in the formation. This includes: (1) the interval from the top of the oil capillary fringe to the oil/air interface in a monitoring well, where oil, water and air co-exist in the pore space; (2) the interval from the oil/air interface to the oil/water interface in a monitoring well, where oil and water coexist in the pore space and the oil may have significant mobility; and (3) the zone below the oil/water interface, where immobile oil may be trapped at residual saturations due to a rise in the water table. Some workers refer to the entire interval described above as the “smear zone”. However, the term “smear zone” has been used by a variety of hydrogeologists and engineers to mean different things. A search of the use of the term “smear zone” on the internet reveals that the term is most commonly applied to the portion of the vertical profile above the water table where variations in the water table elevation has “smeared out” LNAPL in the vadose zone. For example, the U.S. Environmental Protection Agency (Office of Solid Waste and Emergency Response) defined it as;

“Smear zone is the area immediately above the groundwater table, which, in this application, was the area from the top of the well screens to the water table, and which was contaminated by hydrocarbons.”

A similarly common definition was the zone below the oil/water interface in a monitoring wells where LNAPL has been smeared out due to water table fluctuations, such as the following definition;

“ the zone of seasonal or climatic groundwater fluctuation”

Many workers included both of the above intervals in their definition, but in virtually all cases it was stated implicitly or explicitly that the “smear zone” was due to seasonal or climatic water table fluctuations. Because we wish to make it clear that LNAPL is distributed below the water table without any water table fluctuations, and because we are specifically not dealing with the portion of the vadose zone above the oil capillary fringe, we will avoid the use of the term “smear zone”, and simply refer to the vertical interval of interest as the “hydrocarbon impacted interval” or “LNAPL source zone.”

The LNAPL source zone treated is a simplified one, consisting of a rectangular box through which groundwater flows in contact with variable vertical saturations of LNAPL, as determined by the user’s specifications. Unlike most previously published methods, this toolkit considers groundwater transport *through* the LNAPL zone. Groundwater flow is one dimensional with dispersion and reactions in all directions. The geologic medium is homogeneous, as is the distribution of other related fluid and hydraulic properties. Simplified soil layering may also be implemented. Mass balance is accounted for in the partitioning from the LNAPL source to the water and vapor phases – that is, the total LNAPL mass as well as that of each of the soluble constituents within the LNAPL is recalculated for each time step. However, as mass is depleted from the LNAPL through dissolution and volatilization, the distribution (saturations) of the LNAPL is not recalculated from the initial condition, nor is the groundwater flux through the source zone re-calculated as the zone is depleted of LNAPL. Therefore, while the method considers relatively complicated multiphase and multicomponent cleanup and transport issues, it is critically important to remember that the homogeneity and simple dimensionality assumed by the toolkit are generalizations of a much more complicated system. The intended use of the toolkit is to bracket a range of physical and chemical expectations using site specific ranges of data. This manual provides guidance and field back-checks on the key assumptions, where possible.

There are many uncertainties and assumptions involved in use of this toolkit, and the user is cautioned to be fully aware of these before using the results for planning purposes. One prevailing source of uncertainty is site characterization, where generally sparse data sets must be broadly interpreted across the site. It is also common to find key multiphase parameters unmeasured, necessitating user estimation of one or more key factors. It is of fundamental importance to test toolkit assumptions against available field data and site specific parameter measurements to ensure that the scenario outcomes considered are generally realistic. As a conceptual screening tool, part of the analysis process should be to generate realistic conceptualizations of site conditions that can be extended to make site management decisions. Because of the potentially infinite variability in geologic and chemical parameter distributions, the toolkit can only address one set of parameters and distributions at a time. The toolkit is not a numerical model where highly complex site conditions can be reasonably represented. However, even at complex sites, the principles and estimates of the toolkit can be used to bracket a range of risk and cleanup expectations to guide corrective action strategies.

We have touched briefly and generally on the inherent assumptions in this evaluation method. A comprehensive list of assumptions is provided in Section 5, the User's Guide. The assumptions will be better understood once all the linked hydraulics and chemistry factors are described. Realizing that the intent of this method is to assess the benefit of various source treatment actions, it is very important that the assumptions and limitations are fully understood.

2.2 RISK BACKGROUND

Risk is a global term encompassing potential threats from contaminant releases to humans, resources, and the environment. Risk assessment practices allow clear identification of the potential chemical receptors, such as groundwater users, and the protection goals that may be appropriate. Risk is only one basis for setting target cleanup goals, as regulatory standards, public policy, business liability, and other factors may all be relevant. What one does with the concentration estimates derived from the toolkit depends directly on the context of the site and the applicable environmental restoration goals.

Many of the modern corrective action assessment frameworks have streamlined risk assessment practice by integrating site characterization, initial response action, exposure assessment, and risk management (e.g., Risk Assessment Guidance for Superfund, EPA, 1995; Risk-Based Corrective Action, ASTM, 1995). Regardless of the framework used, most quantitative risk assessment is based on four main components:

1. Hazard identification entails a qualitative assessment of site conditions and operating history to identify potential compounds of concern. For typical gasoline station operations, these compounds could include aromatic hydrocarbons and fuel oxygenates such as methyl tertiary-butyl ether (MTBE).
2. Dose Response entails defining the chemical hazard and toxicologic properties of the compounds of concern identified in the previous step. The result is a quantitative relationship between chemical dose and potential health hazards for either acute or chronic effects.
3. Exposure Assessment involves assessing the potential contaminant receptors and calculating the potential chemical concentrations at receptor points of contact. Receptors can include both people and environmentally sensitive habitats and animals. Chemical fate and transport calculations are included in this component. The points of contact often coincide with regulatory points of compliance.

4. Risk Characterization is the quantitative synthesis of the preceding steps under which the nature of the contaminant, its pathways, and receptors are combined to estimate specific risks of potential deleterious effects from the contaminant release.

Of the four risk assessment components above, exposure, chemical fate and transport (F&T), and remediation assessment often have the widest latitude for site specific scientific evaluation. This is because both hazard identification and dose response aspects are derived from epidemiological studies characterizing the potential environmental impacts to humans and other receptors of various chemical compounds. These studies are often statistically difficult and may involve inferences from one receptor to another that may or may not be valid in all instances (e.g., mice to people). Toxicologic studies are also time consuming and expensive and open to significant interpretation. Therefore, the general practice is to use standard chemical toxicity information provided by the U.S. EPA or other qualified sources.

For the reasons discussed, the degree of risk for a given site strongly depends on the results of receptor and fate and transport evaluations. Fate and transport evaluations are also the cornerstones of remediation planning and system design, since natural and artificial transport (i.e., cleanup) are both controlled by the same processes. This is reflected in the remediation selection aspects of risk-based frameworks.

When a risk reduction is suggested to be necessary, or when target thresholds are exceeded, the chemical concentrations reaching receptors must be reduced, or pathways eliminated, and methods should be selected based on their capability to effectively reach the desired goals. Risk reduction and current cleanup technology are often not synonymous because cleanup limitations often preclude significant risk reduction. In these cases, other risk management techniques are as protective of environmental and human health. The focus of this work is to aid users in deciding if common cleanup technologies will meet the site specific risk-based goals or other targets that may apply.

HYDROGEOLOGY OF LNAPL FLOW IN THE SUBSURFACE

The fundamental principles of LNAPL hydraulics are identical to basic groundwater hydrogeology, but the devil is in the details. The differences between the flow of a single fluid in porous media and the flow of multiple fluids in the same media are significant, and directly impact mobility, recoverability, and risk associated with all phases (water, air, LNAPL). Every complexity of standard hydrogeology is magnified by the presence and interaction of multiple fluid phases. Often these effects are synergistic. For example, where there is a three order of magnitude range in the mobility of water between a medium-grained sand and a silt, there will be as much as a six order of magnitude difference in the mobility of an LNAPL under typical conditions. In the interest of time and sanity, we have attempted to bring some of the most salient concepts together in this section about LNAPL hydrogeology. Since whole volumes of work are dedicated to the subject, it is obvious that we must skip over many of the finer points in order to develop the technical story required to make this toolkit work. The bibliography scratches the surface of the works available in multiphase fluid mechanics and related disciplines; for those wishing more insight, however, it is a good place to start.

The main points of multiphase fluid hydrogeology can be highlighted in a few sentences, and are therefore not conceptually difficult. (1) Fluids flow downgradient – LNAPLs and water frequently have different gradients and gradient directions, so directions of groundwater movement and LNAPL movement must be assessed separately. (2) For a fixed set of fluid pressures, the size of the pore space controls the relative percentage of the pore space (phase saturation) occupied by each fluid – LNAPL and air displace water more readily from large pore spaces than from small pore spaces. However, once LNAPL has invaded a small pore space, it is more difficult to displace it with water than from a large pore space. (3) Fluids flow less readily when other fluids block their way – as LNAPL saturation increases, the mobility of LNAPL increases and the mobility of water decreases.

These are several of the key concepts necessary to build an understanding of multiphase flow. The following sections provide the individual pieces that link a description of the LNAPL source distribution to chemical transport from that source.

3.1 DISTRIBUTION OF LNAPL, WATER, AND AIR

The first controls of importance in the problem are the distribution of LNAPL, water, and vapor in the pore space. From these distributions come the mass of the impacts in the conceptual zone of interest, the relative mobility of each phase in the presence of others, and related factors like residual saturation. The following sections develop the fundamental hydraulics of multiphase fluid conditions.

3.1.1 Capillary Theory

The first subject deserving consideration in a multiphase fluid system is how to describe the distribution of the various phases (LNAPL, water, and air) in the subsurface. Granular soil may be viewed as an assemblage of tortuous pore tubes. In any small pore, capillary forces are usually a key element to the distribution of multiple phases in that pore, and therefore can be expected to play a critical role in multiphase hydraulics. Capillary forces are derived from the attraction of the surface of a liquid to the surface of a solid, which either elevates or depresses the liquid depending upon molecular surface forces. For most silicate granular soils, water rises in pore spaces in proportion to the interfacial tension of the water and inversely with the pore throat diameter, as discussed below. We will develop key concepts using the capillary tube analogy, and expand from there to natural granular soils. Only background is provided here; more expansive treatments can be found in the bibliography to this report (key capillary equations are in Appendix A).

Capillary tubes are a well-known physics/chemistry experiment. When a small diameter glass tube is placed in an open water bath, the water will rise in the tube due to capillary forces (Figure 3-1) exerted by the interaction of the pore wall material with water molecules (for this example). Since the water level in the bath is at atmospheric pressure, as is the surrounding air, it follows that the water that has risen in the tube must be held under tension. The capillary pressure at the top of the water column will be a function of the radius of the capillary tube (r) and the air-water interfacial tension, or surface tension (σ_{aw}), as given by $P_c = 2\sigma_{aw}/r$. Capillary head, or equivalently the height of the water rise (h_c) in the capillary tube, is simply the pressure divided by the unit weight of water, or $H_c = 2\sigma_{aw}/\gamma_w r$. Therefore, the capillary pressure and the height of capillary rise in a pore space are proportional to the interfacial tension and inversely proportional to the pore throat radius.

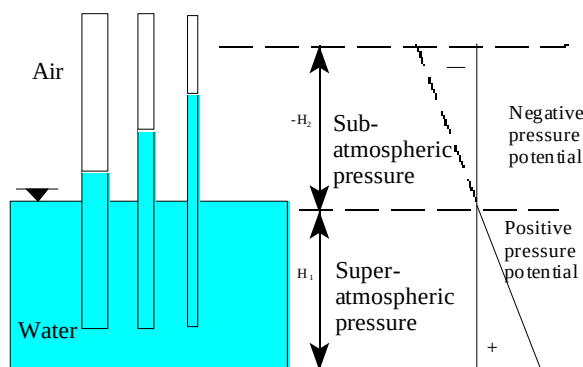


Figure 3-1. Schematic of a capillary tube bath. The water in the tubes is less than atmospheric above the open water table of the bath.

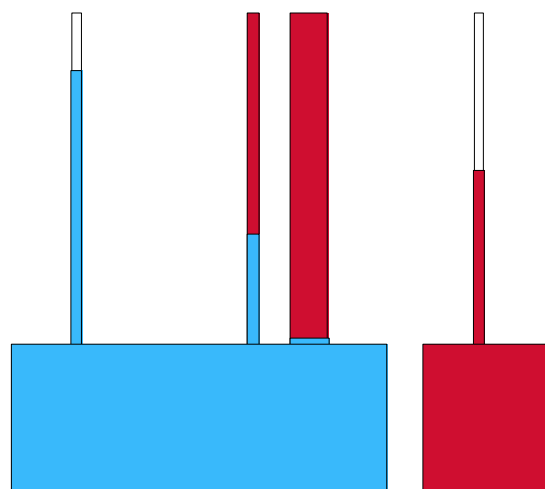


Figure 3-2. Capillary bath for 3 fluid phase couplets, water in blue, oil in red, air in white.

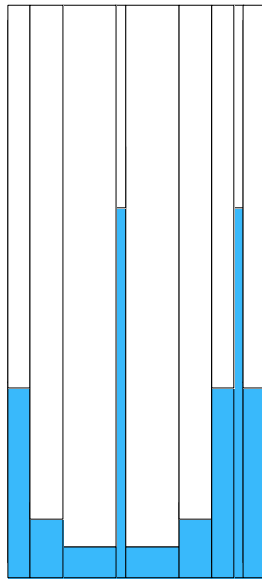


Figure 3-3. A schematic of mixed capillary rises for different pore-throats (i.e., tube sizes). In typical soil, a variety of pore-throat sizes are present resulting in this kind of variable saturation distribution.

Water and air, like water and LNAPL and LNAPL and air are immiscible, so it is not surprising to find there is analogous capillarity to LNAPL/water and LNAPL/air systems (Figure 3-2). In fact, the capillary pressure at the LNAPL/water (P_c^{ow}) and LNAPL/air (P_c^{oa}) interfaces in a capillary tube of radius r can be scaled to the capillary pressure at the air/water interface by recognizing that $P_c^{ow} = 2\sigma_{ow}/r$ and $P_c^{oa} = 2\sigma_{oa}/r$, where σ_{ow} and σ_{oa} are the oil-water and oil-air interfacial tensions, respectively. Because the radius r is a common factor, all capillary couplet systems can be related and scaled to a common system, usually the air-water system for convenience.

Extending these principles, soil can be viewed schematically as a suite of tortuous capillary tubes of differing pore diameters, with each size “packet” causing a different capillary rise (Figure 3-3). The usual graphical representation of the pore throat distribution (or capillarity) is often called the soil characteristic curve, the shape of which depends on the distribution of pore sizes for each soil (Figure 3-4). At equilibrium in a homogeneous media, these curves represent the water content as a function capillary pressure, or equivalently for the water-air couplet, elevation above the water table. As one moves upward in elevation above the water table (i.e., increasing capillary pressure), only the

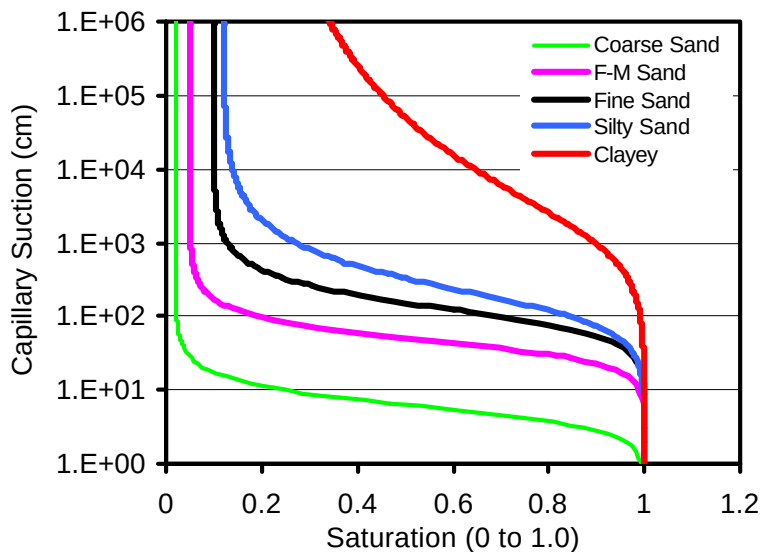


Figure 3-4. Capillary characteristic curves for typical soils. The curves represent the distribution of pore throat sizes.

smaller pore throats hold water and the average moisture content decreases as air saturation increases.

As long as the fluid phases are continuous, the relative saturation of each is controlled by the capillary pressure and pore radius distribution. Capillary pressure (P_c) is simply the difference between the fluid pressure of the nonwetting fluid (P_{nw}) and the fluid pressure of the wetting fluid (P_w), or $P_c = P_{nw} - P_w$. Intuitively, if one applied enough driving force to a nonwetting fluid, such as air or LNAPL, the nonwetting fluid could

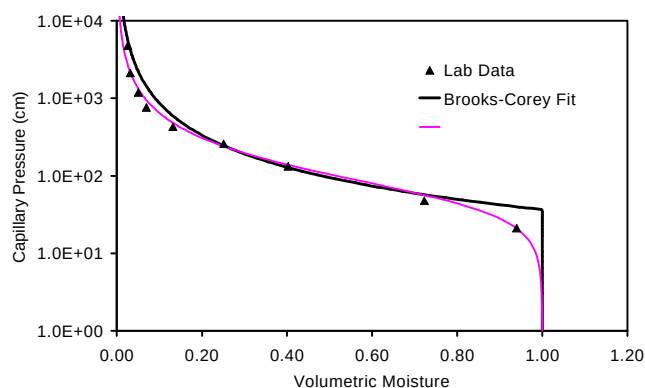


Figure 3-5. Lab data & best fit curves using both Brooks-Corey and van Genuchten models.

displace water from any pore space. But under natural conditions, it is observed that soil pore distribution has a significant impact on LNAPL, water, and air saturation under any pressure or gradient regime.

Given the description above, one can sense that high permeability materials with generally larger pore throats typically hold less capillary water (a small capillary fringe) than low permeability materials (a large capillary fringe) under equilibrium or for the same

gradient conditions. These capillary descriptions of fluid saturation are the underpinning of all the remaining linked multiphase theory. As might be expected, complications to capillary properties and theory occur in soils with clays that shrink and swell, fractured materials, in pore structures undergoing certain types of chemical alteration, and under other atypical conditions. These conditions can result in a pore matrix that varies with time, making quantitative capillary description difficult. The interested reader is directed to the bibliography for other works touching on capillary theory and complexities.

It is worth mentioning that two commonly used capillary models differ in a key underlying assumption. The Brooks-Corey (BC) capillary function assumes a sharp capillary fringe height (step function) and a threshold immiscible phase entry pressure (Figure 3-5; Appendix A). That is, below a certain capillary pressure, it is assumed that water (or another wetting phase) will not be displaced or intruded by the nonwetting fluid. The van Genuchten (VG) function is continuous, and assumes that displacement of water by a nonwetting phase is possible at small capillary pressures, though the corresponding saturation of the nonwetting phase may be very small. It has been our experience, based on fitting many lab-derived capillary data sets (e.g., Figure 3-9), that the VG function generally provides a more representative fit, but there are cases where the BC function does an equally good and sometimes better job. The functions essentially converge for conditions where the “pore entry pressure” is exceeded, but vary significantly at pressures below the theoretical entry pressure value. This may not seem particularly important, but it has strong ramifications to the expected distribution of hydrocarbon in the source zones and the linked flow and chemical transport conditions. In this work, the VG capillary equation is used since the BC equation is essentially equivalent except at low pressures. One exception to this is the incorporation of an analytic hydraulic recovery screening model by others that uses the BC function (Charbeneau, 1999), as will be discussed in following sections with supporting equations in Appendix B.

We have noted above that all immiscible fluid couplets (e.g., LNAPL/water, water/air, air/LNAPL) respond to capillary forces in proportion to interfacial tension and pore throat radii. For the case we are considering, water, LNAPL, and vapor coexisting in the aquifer and capillary zone, capillary definition is needed for each couplet system. It has been observed that the soil capillary curves and properties are generally scalable between fluid pairs by the ratio of the interfacial tensions between the couplets of interest (Leverett, 1941; Parker, 1987). Often, lab measurements of capillarity are performed using air and water for agricultural and geotechnical applications, or measurements using air and mercury in some oil reservoir work. Each of the different test methods generates a two-phase capillary curve that represents the underlying pore throat distribution and fluid retention as a function of capillary pressure. These relationships can be scaled to other couplet systems using the interfacial tension ratios so that all three capillary couplets of interest here are defined (Figure 3-6; equations in Appendix A).

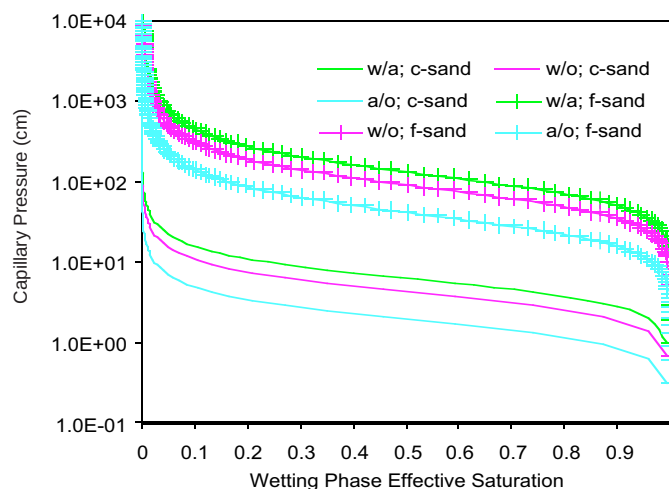


Figure 3-6. Characteristic capillary curves for 3 phase couplets in 2 sands. The shapes are identical, the offsets caused by the differences in interfacial fluid tension (IFT) and fluid density.

3.1.2 Distribution of Fluids Under Vertical Equilibrium

The relationships above can be extended to estimate field fluid saturation of LNAPL, water, and air in the capillary and water table regions. The sections below will first develop these relationships for homogenous soils, and then discuss how the same principles may be applied to heterogeneous systems. The full mathematical development is provided in Appendix A.

3.1.2.1 Homogeneous Soils. For environmental conditions, it has been observed that if sufficient time is allowed for the LNAPL to come to vertical equilibrium (VEQ) the LNAPL thickness observed in a well can be used to determine the capillary pressure relationships between the various phases (Farr et al., 1990; Lenhard & Parker, 1990). VEQ implies the vertical gradient in each phase (water/LNAPL) is zero throughout the mixed saturation profile. That is, there is no vertical gradient for LNAPL or water to move vertically in the equilibrated system. In such a system, the oil-water capillary pressure (P_c^{ow}) is zero below the oil-water interface in the formation or monitoring well, and is a function of the relative density of the LNAPL ($\rho_{ro} = \rho_o/\rho_w$), where ρ_o is the LNAPL density and ρ_w is the density of water and the height above the oil/water interface (h_{ow}). Similarly, the oil/air capillary pressure (P_c^{oa}) is zero below the oil/air interface in a monitoring wells and is a function of

the LNAPL relative density and the height above the oil/air interface (h_{oa}). These capillary pressures under VEQ, respectively, are: $P_c^{ow} = (1 - \rho_{ro}) h_{ow}$ and $P_c^{oa} = \rho_{ro} h_{oa}$.

Once capillary pressure is defined, it is combined with capillary soil and fluid properties to result in the saturation profiles of each wetting phase of interest (Fig. 3-7). This is analogous to oil/brine/gas boundary relationships defined in the oil production industry (Bradley, 1987; Chatzis et al., 1983). Specifically, above the

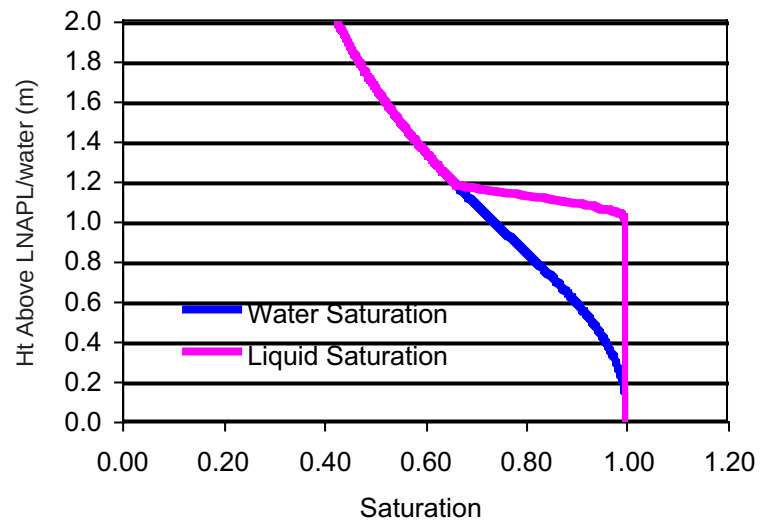


Figure 3-7. Wetting phase saturations, water below the LNAPL/air interface in the formation for 1 m of equilibrated LNAPL, and total liquid saturation above. The sum of all phases (air, water, LNAPL) is always 1.0, so by subtraction, all saturations can be defined.

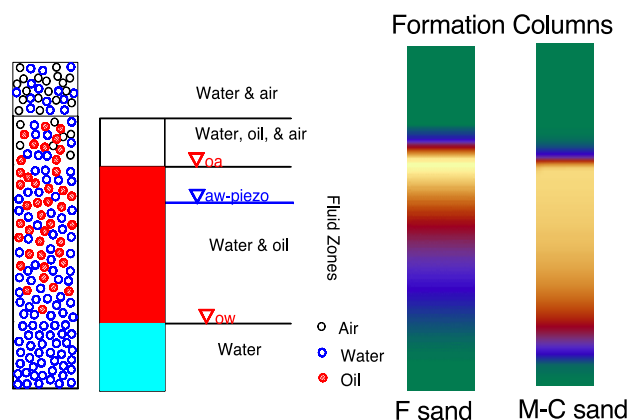


Figure 3-8a. Schematic of pore and well distribution of free product (after Farr et al., 1990) and calculated formation saturation columns.

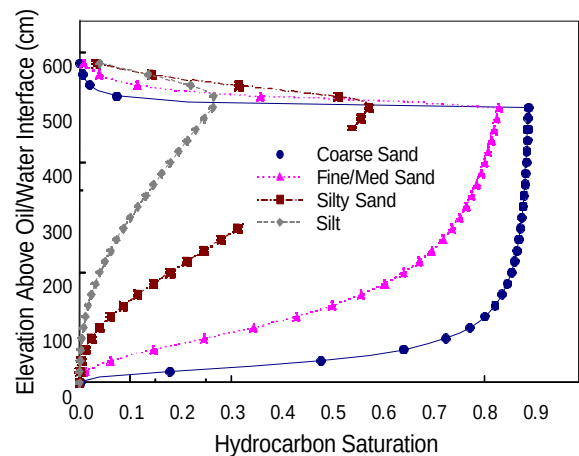


Figure 3-8b. Oil saturation estimated for various soils based on capillary properties and VEQ for 500 cm thickness.

oil/water interface and below the “oil table”, the water (wetting phase) and LNAPL (nonwetting) saturation is controlled by the LNAPL/water capillary pressure. Since the total saturation = 1.0, the LNAPL saturation is simply $1 - S_w$. Above the oil/water liquid table, the liquid (S_l) and air saturation (LNAPL & water) are controlled by the oil/air capillary pressure. The air saturation is $(1 - S_l)$. From these definitions we can now describe the equilibrium LNAPL saturation profiles in the formation for any known set of soil, fluid, LNAPL thickness and associated capillary pressure conditions (Figures 3-8a & b). These profiles are usually plotted as height above the LNAPL/water contact because this is the datum where the capillary pressure differential begins. Keep in mind that this elevation is not the same as, but simply related to, the capillary pressure (see equations above, and in Appendix A).

The capillary relationships are exponential, and therefore very sensitive to soil type (pore size distribution) and equilibrated LNAPL thickness, or equivalently the LNAPL pressure head in the formation. In fact, as will be demonstrated subsequently, capillary properties are more important than intrinsic permeability or hydraulic conductivity. Because of this sensitivity, site-specific values of capillary properties are important in the analysis. Direct measurement of those capillary properties is preferable to values inferred from soil texture descriptions.

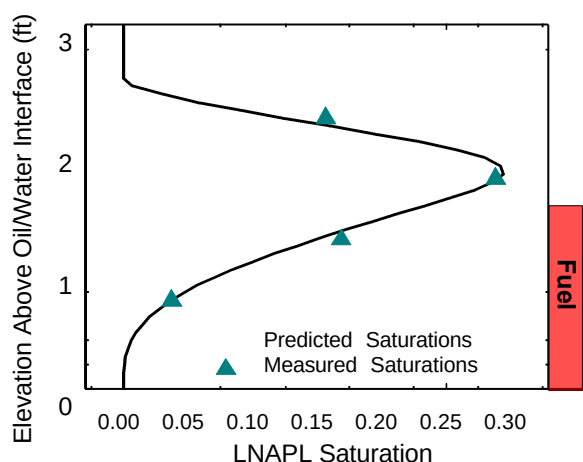


Figure 3-9a. Comparison of the capillary model to fuel saturation data collected at a dune sand site.

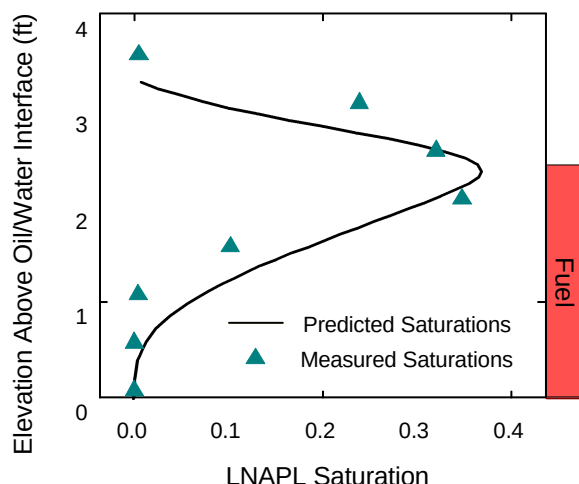


Figure 3-9b. Saturation data from the same site, but with a larger observed well thickness.

Experience has indicated that where the hydrostatic equilibrium assumption is satisfied, field and lab measurements strongly agree with capillary theory (Figures 3-9a and b). Like any sound physical

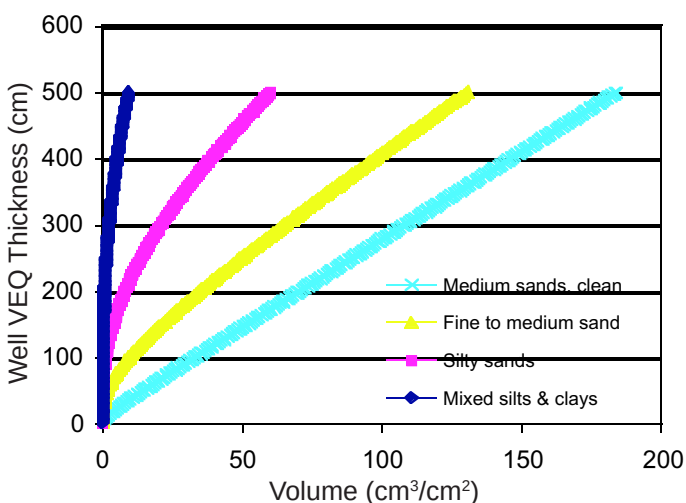


Figure 3-10. Integrated VEQ formation LNAPL volume as a function of theoretical observed well thickness for several soils.

model (and this model has 50 years of practical oil field use to back it), when the assumptions are met, the principles explain real observations. In contrast, several published lab experiments appear on the surface to conflict with capillary theory applied to environmental situations until one recognizes that the necessary VEQ boundary conditions have not likely been satisfied (e.g., Ballesterio et al., 1994; EPA, 1995). Again, capillary theory has worked well for decades in the petroleum industry, and the analogy to environmental LNAPL conditions is fairly clear (Jennings, 1987; Farr et al., 1990). While disequilibrium

conditions clearly complicate matters, as will be discussed subsequently, capillarity remains a fundamental cornerstone of fluid mechanics and is required to explain virtually any multiphase condition. Like all scientific endeavors, improvements to the theory are expected through time but, without a doubt, phase saturations are related to pore size distributions, fluid properties, and fluid pressures.

Perhaps the easiest way to picture the in situ LNAPL “floating within” the water table is by analogy to an iceberg. Most people recognize that the iceberg is 90% submerged because ice is less dense (0.9 g/cc) than water (1 g/cc). For an LNAPL thickness at equilibrium with a density of 0.75 g/cc, about 25% of the thickness will be above the water table, and 75% below. However, because the smaller pores will retain water against the weight of the LNAPL, the displacement in soil is volumetrically less than 100%. So, while there is no thickness exaggeration, there is an apparent volume exaggeration between observed thicknesses and volume in the formation. The volumetric fraction of LNAPL at and below the water table is strongly dependent on soil capillary characteristics, with coarser soils usually have much larger sub-water table impacts than fine materials (e.g., Figures 3-7 through 3-10).

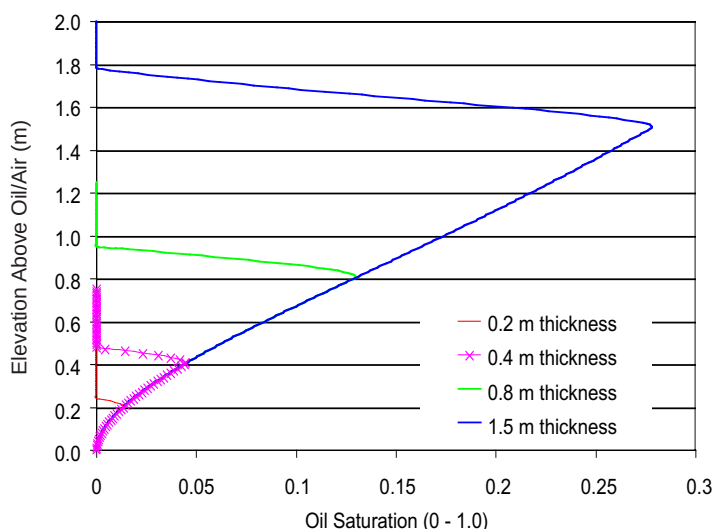


Figure 3-11. LNAPL saturation profiles for different equilibrated thicknesses in a silty sand showing nonlinear dependency on capillary pressure as related to thickness.

The LNAPL saturation profile in the formation, when vertically integrated, provides a volume per unit area which, as we have seen, depends on the capillary pressure (or correlated equilibrated thickness) and the capillary properties (Figures 3-10 & 3-11; Appendix A). The area integration of the LNAPL volume per unit area estimates for all wells in a plume exhibiting free product results in an estimate of the total plume volume. Be aware that if the system is not under ideal VEQ conditions, or if there is a significant “smear” zone, the volume estimate will be in error, as is discussed later. Also recognize that since the local area volume is reported in units of volume per unit area (e.g., ft³/ft²; cm³/cm²; gal/ft², etc.), the dimensions reduce to units of length. This is often misinterpreted as a thickness exaggeration, which it is not. The data and theory covered above clearly show that the LNAPL-impacted vertical interval is always greater than the equilibrated thickness observed in a monitoring well under VEQ conditions. This is critically important because the volume of impacted aquifer material, as well as the LNAPL distribution within that volume, are key controls over cleanup, dissolution, biodegradation, and risk. Note that there are field conditions where product can be perched and a thickness exaggeration is possible due to the well acting as a local drain, as well as transient (non-equilibrium) conditions where thickness exaggeration is also possible.

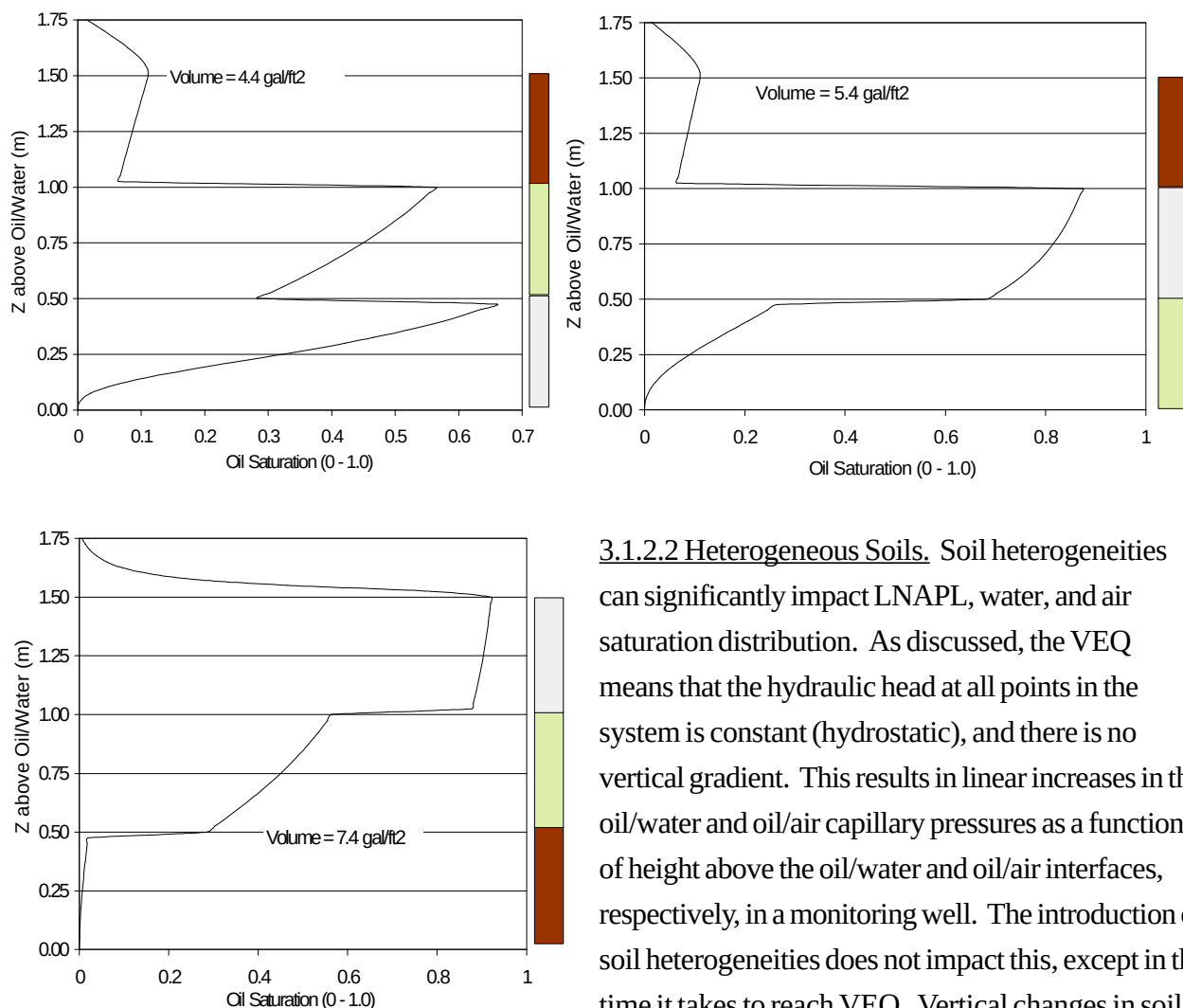


Figure 3-12a, b, and c. The VEQ distribution of gasoline as a function of stratigraphic position through the LNAPL zone. Medium sand = speckled; fine sand = white; silty sand = grey.

3.1.2.2 Heterogeneous Soils. Soil heterogeneities can significantly impact LNAPL, water, and air saturation distribution. As discussed, the VEQ means that the hydraulic head at all points in the system is constant (hydrostatic), and there is no vertical gradient. This results in linear increases in the oil/water and oil/air capillary pressures as a function of height above the oil/water and oil/air interfaces, respectively, in a monitoring well. The introduction of soil heterogeneities does not impact this, except in the time it takes to reach VEQ. Vertical changes in soil capillary properties, however, result in a heterogeneous LNAPL distribution. This heterogeneous fluid saturation profile can be calculated simply by using the capillary pressure calculated under VEQ and the appropriate soil

capillary curve for each soil type in the vertical sequence. For most vertically heterogeneous sequences, the maximum saturation and mass are controlled by the coarsest beds (lowest capillarity), although vertical position in the impacted zone can be important. For instance, if we juxtapose three beds of different soil types and equivalent thickness (0.5 m; Figures 12a-c), we see that the LNAPL saturation profiles vary significantly as a function of position. The soils contrasted are a clean medium-grained sand, a fine-sand, and a silty sand. Notice that the formation LNAPL distribution varies significantly depending on the ordering of the beds, and that the total volume associated with each stacking is different. The greatest volume is where the medium sand is at the top of the LNAPL column, resulting in about 7.4 gals/ft² under the curve.

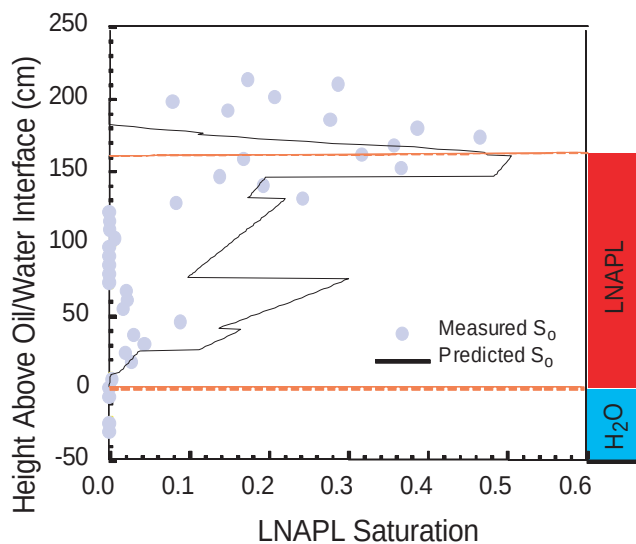


Figure 3-13a. Predicted versus measured LNAPL profile in an interbedded sand and silty sand formation in San Diego (Huntley et al., 1994). Note transient stranding above the current liquid table.

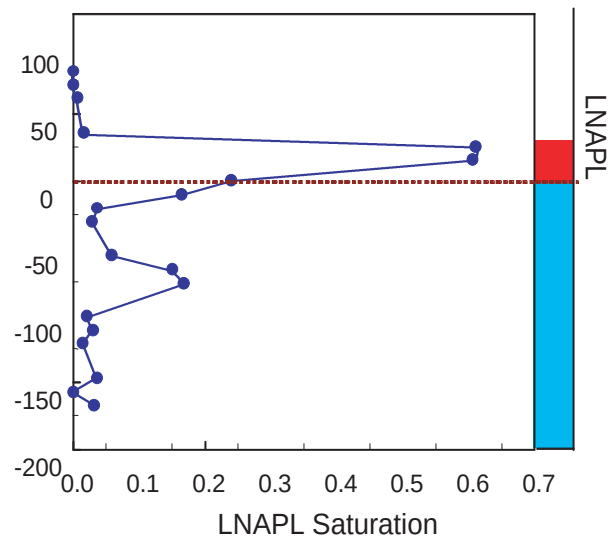


Figure 3-13b. Measured LNAPL saturation in a fine sand following a rise in the water table. Note stranding below the water table, and transient compression of the small thickness LNAPL zone.

It is useful to look at heterogeneous field conditions for comparison to theory. A detailed field study (Huntley et al., 1994) of fuel distribution in a widespread LNAPL plume showed that LNAPL distribution was strongly controlled by the vertical distribution of capillary properties relative to observed LNAPL in observation wells (e.g., Figure 3-13a). The example site exhibited highly variable LNAPL saturations that were generally, but not specifically, represented by the capillary model. The LNAPL saturation and soil data indicate there is a tendency for coarser materials to more closely match the capillary predictions than fine-grained materials. Although more study is needed, a logical explanation for this observation is that fine-grained materials require significantly longer equilibration times, and in

practicality may never equilibrate fully. Similarly, one also finds “stranding” or “entrapment” of LNAPL below the water table in the field after the water table has risen (Figure 3-13b). This effect is caused from hysteresis and disequilibrium effects and contrasts in the effective conductivity of the water versus the LNAPL (discussed subsequently).

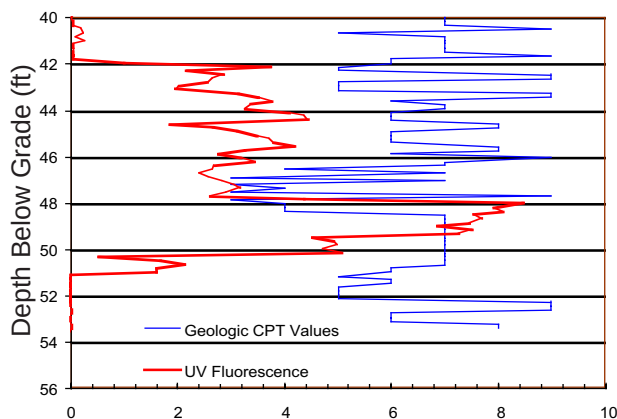


Figure 3-14. Downhole cone penetrometer and fluorescence logging showing inch-scale variability in geologic properties and LNAPL saturation (proportional to fluorescence log).

We see these same occurrences in indirect measurements of saturation, such as induced laser or ultraviolet fluorescence logging (Figure 3-14). In fact, geophysical logging may be one

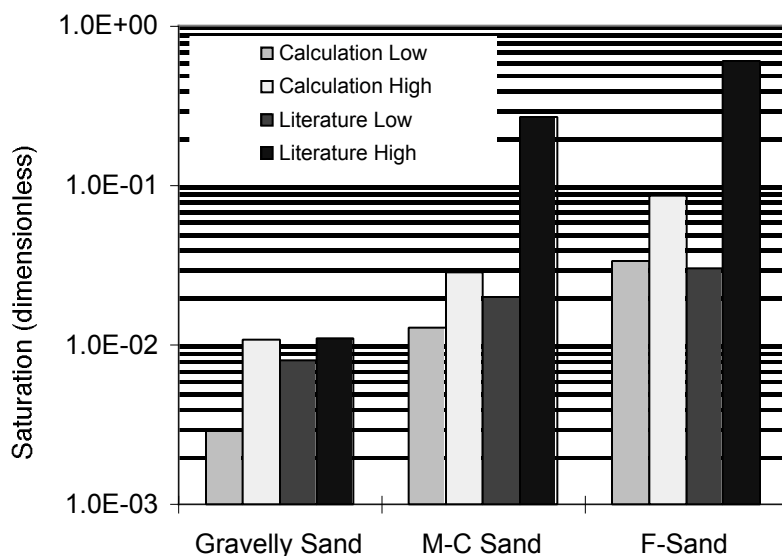


Figure 3-15. Range of residual gasoline saturation for 3 soil types (from Mercer & Cohen, 1990). Calculated ranges from Parker (1987; see Appendix A).

of the few techniques capable of cost-effectively detailing small-scale variability in geologic bedding and LNAPL distribution. In any case, when conditions are heterogeneous, expect idealized equilibrium capillary theory to encounter difficulties, not because the theory is flawed, but rather because thorough definition of the system is difficult and equilibrium is often not established. As shown above, if the scale of interbedding is known, heterogeneous LNAPL saturation profiles

can be estimated. This is one option

available for the LNAPL source description in the accompanying software utility, which is then used for calculations of groundwater dissolution and volatilization. Keep in mind that equilibrium conditions, by definition, do not account for complications of water table fluctuation and other transient LNAPL migration events. The vertical equilibrium assumption should be invoked and trusted only when justified by field conditions and data.

3.1.3 Hysteresis and LNAPL Entrapment

The capillary characteristics discussed above focus on the relations between capillary pressure and LNAPL saturation under conditions where LNAPL is displacing water from pore space, that is where LNAPL is invading a water saturated area. Important differences occur when the reverse happens,

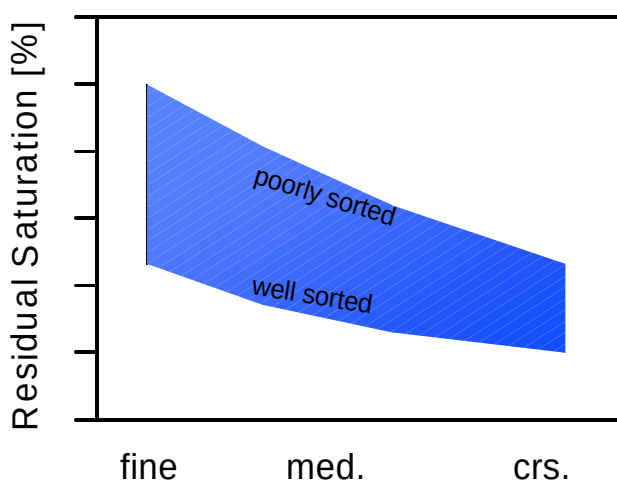


Figure 3-16. Schematic from available data ranges for residual LNAPL saturation in reservoir materials showing dependency on sorting and tortuosity.

when water displaces water from pore spaces, such as occurs during any hydraulic remediation or water flooding exercise. Laboratory and field measurements indicate that porous media have a relatively large capacity to hold fluids, including LNAPL, against natural drainage forces. For instance, in water driven oil reservoir conditions, it is common for retained LNAPL to be present at saturations, called residual saturations, from 20 - 60% (in Bradley, 1987). Residual gasoline saturation in sands has been documented to range from as low as 2% to as high as 60% under a range of

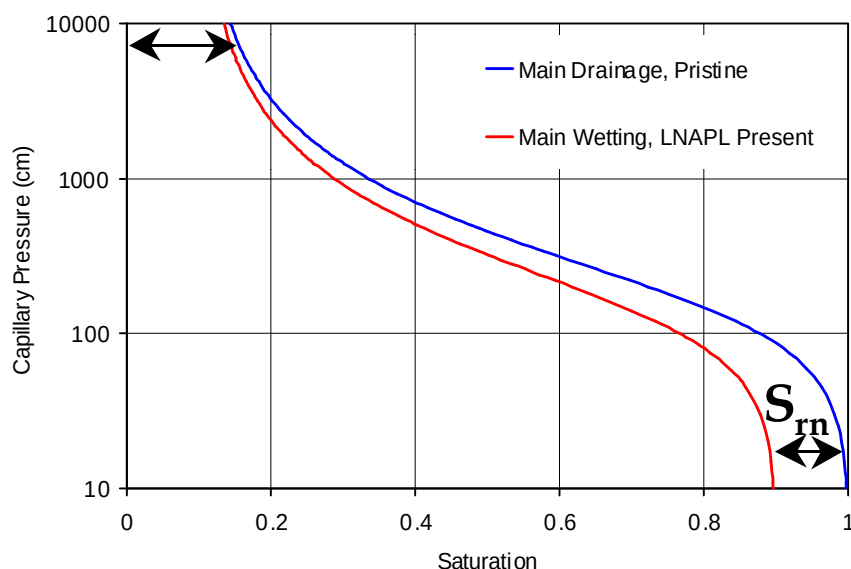


Figure 3-17. Scanning capillary curves showing the hysteresis (path dependency) effect for the wetting phase (water) displaced by LNAPL. Residual LNAPL saturation (approximately 15% in this case) fills pore space formerly occupied by water in the pristine system. The curves are plotted against capillary pressure head (cm) of the LNAPL/water system.

lab and field conditions (Figure 3-15; Mercer & Cohen, 1990).

Residual saturation tends to increase as soil becomes finer-grained, porosity decreases, and pore heterogeneity increases (Figure 3-16; Beckett & Lundegard, 1998; Chatzis et al., 1983).

The LNAPL interfacial tensions and viscosity can also have some effect.

Because of a limited environmental database, it is necessary to combine the residual saturation findings from agriculture and petroleum production to broaden the range of applicable values. Databases

of LNAPL parameter values are needed to assist in further constraining the range of residual saturation for environmental conditions.

The explanation for residual saturation lies in the complexity and tortuosity of discrete pore pathways and the closely related concepts of hysteresis and entrapment. As a result, the capillary curve controlling water saturations are different for LNAPL displacing water (Drainage curve, Figure 3-17) compared to water displacing LNAPL (Wetting curve, Figure 3-17). This difference between the wetting and drainage curves is called hysteresis, and has been documented for many decades in agricultural (Stephens, 1996; Corey, 1986). The most important implication of hysteresis to the

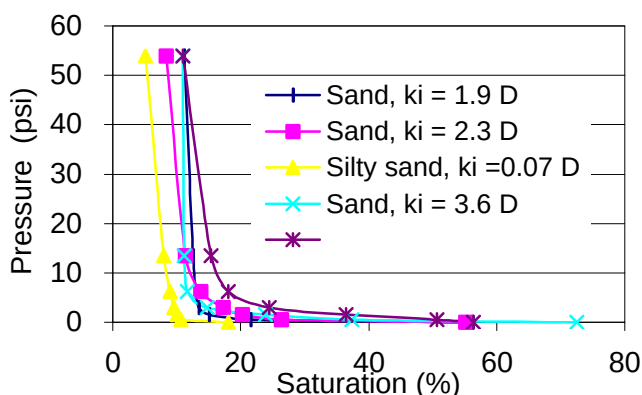


Figure 3-18. Lab measurements of LNAPL saturation versus applied pressure for different soil (permeability given in Darcys [D]); endpoints are residual LNAPL saturation, field LNAPL capacity is somewhere near the inflection of the curves.

subject at hand is that the re-wetting curve (Figure 3-17) never achieves a water saturation of 1.0. This means that no matter what fluid pressures are applied in a water flooding operation, or how long we attempt to recover LNAPL hydraulically, water will not displace all of the LNAPL from the pore space, resulting in entrapped residual LNAPL. The difference between the maximum water saturation under drainage conditions (1.0) and the maximum water saturation under re-wetting (Figure 3-17) is the nonwetting phase residual saturation (S_{rn} , Figure 3-17). The entrapment occurs because the continuous pore pathways for

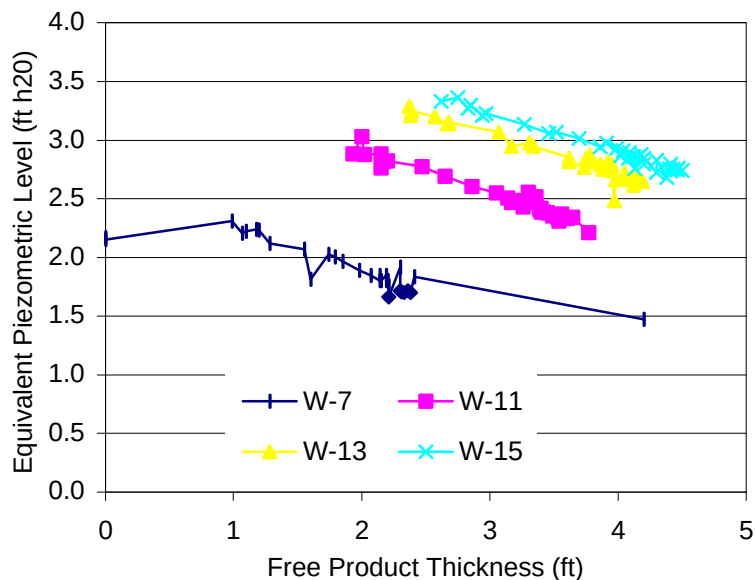


Figure 3-19. Data showing the inverse relationship between free product thickness and piezometric pressure over six years of monitoring. The individual measurements are from variable times, as shown in Figure 3-20.

value due to the influence of field scale heterogeneity. Heterogeneity can trap LNAPL in zones where, although present above true residual, it is immobilized by the surrounding materials. The field residual saturation is the best-case endpoint of any hydraulic recovery scheme, and is a key factor used in cleanup and chemical depletion calculations herein.

Lab measurements of “residual LNAPL saturation” are variable and may not really measure the hysteresis effect that causes true residual saturation. Drainage of LNAPL from core samples to

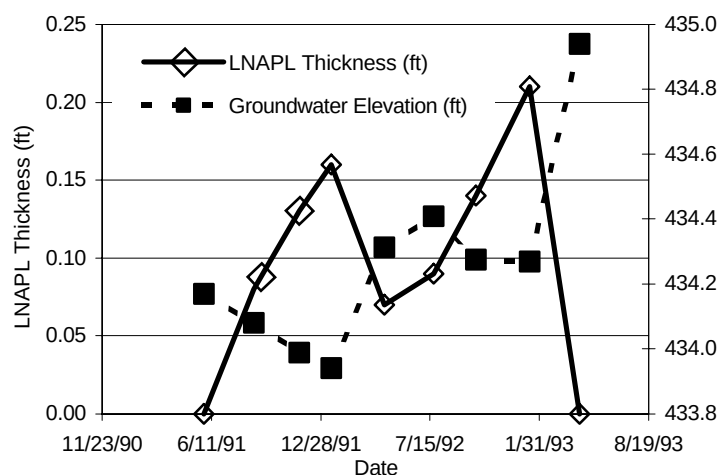


Figure 3-20. Data showing time series graph of product diminishing and increasing dependent simply on groundwater elevation.

LNAPL get cut off when the LNAPL saturation falls below a certain threshold. Not surprisingly, the more heterogeneous the pore or grain-size distribution, the greater the LNAPL stranding capacity of the particular soil (Figure 3-15). Nor is it surprising that the residual LNAPL capacity is often greater in the saturated zone than in the vadose zone (Lenhard & Parker, 1988).

It is important to distinguish between true residual LNAPL saturation, which is a lab measurement under ideal two-phase conditions, and ***field residual saturation***, which is invariably a larger

residual saturation is generally very slow. Therefore, labs may estimate “residual LNAPL saturation” under an induced pressure gradient (e.g., centrifugation, pressure permeameters, etc.). Many of these tests are 3-phase, with air under pressure used to drive both water and LNAPL out of the pore space. These tests allow rapid screening of retained LNAPL under these conditions, but are not a true residual measurement (e.g., Figure 3-18). True residual LNAPL saturation values are usually larger, so this variety of lab values called “residual saturation”

should be used with caution. These types of measurements are of value for evaluating vadose zone residual (a 3-phase system) saturations and air-based cleanup schemes where vacuum or pressure is applied.

In addition to the residual saturation controlling the best-case endpoint to remediation using hydraulic approaches, the concept of residual saturation has significant implications with respect to the distribution of LNAPLs in the subsurface under conditions of a rising water table. Once LNAPL has invaded a pore space, increases in the fluid pressure of the wetting phase, such as that produced by a rising water table, will act to displace LNAPL out of that pore space. This displacement of LNAPL by water is, again, limited by the residual saturation of the LNAPL. Therefore, a rising water table will act to entrap LNAPL below the oil/water interface in a monitoring well, producing what many workers refer to as a “smear zone”. This process is enhanced by the low mobility of LNAPL compared to that of water, as will be discussed later.

This LNAPL entrapped via this mechanism will not be amenable to any form of hydraulic remediation, but will contribute significantly to the dissolved-phase plume downgradient of the source area. This is a significant impact in areas where water tables have risen due to basin management or natural hydrologic system changes. For instance, in Southern California, salt water barrier projects and changes in basin pumping have caused groundwater levels to rise several tens of feet in some areas, stranding significant quantities of product below the current water table. In addition, if the surface source of an LNAPL has been eliminated, this rising water table will redistribute a fixed mass of LNAPL over a larger vertical interval, resulting in a decreased thickness of hydrocarbon in a monitoring well (Kemblowski & Chiang, 1990). The result is that LNAPL thickness can vary significantly with changes in groundwater elevation. We often observe that free product thins or “disappears” from observation wells with even modest rises in the water table, only to reappear when the water table falls (e.g., Figures 3-19 and 3-20). This is a good example where the presence of, or lack of, observable free product in a well is often irrelevant to risk, since under these “stranding” conditions the source for risk is unchanged. As we will see, the change in product thickness in observation wells is, of itself, often a poor indicator of risk or risk benefits associated with cleanup efforts.

3.1.4 Implications of LNAPL, Water, and Air Distribution

The mass and distribution of LNAPL is the control over rates of dissolution and source longevity. Though the equilibrated thickness of LNAPL in an observation well is always less than the thickness of the impacted aquifer zone (no thickness exaggeration), the volume of LNAPL in the formation is always less than that indicated by the equilibrated thickness in the monitoring wells and the formation porosity (volume exaggeration). Therefore, the formation LNAPL volume is smaller and the volume of impacted aquifer material larger than implied by the thickness of LNAPL in a monitoring well.