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 (**LN**APL Dissolution **a**nd Transport **S**creening **T**ool). 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.
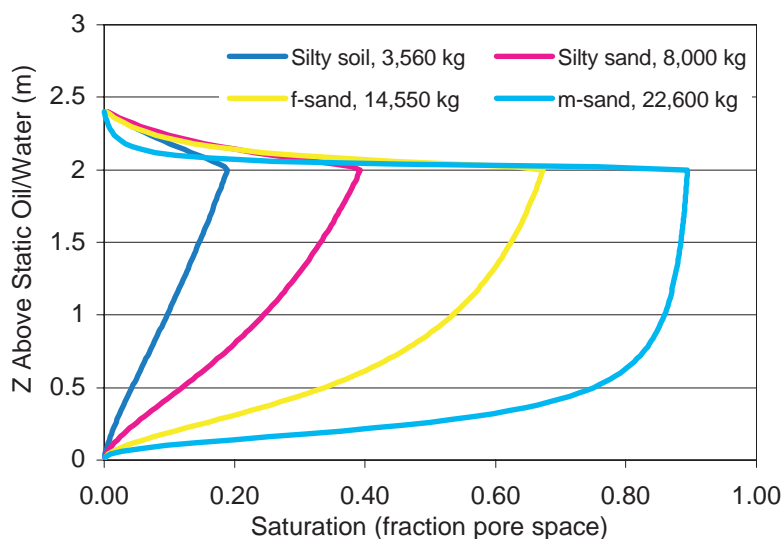
The Effect of Soil Type

Figure E-1. Gasoline saturation curves for 2 m observed well thhickness 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
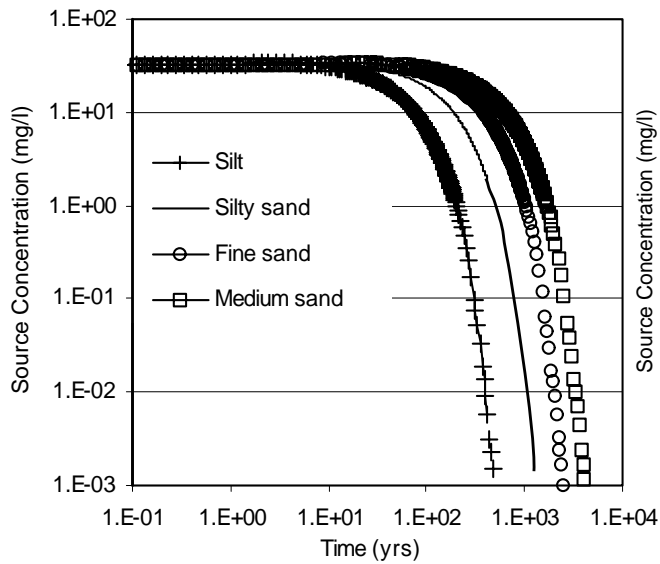
Figure E-2a. Source depletion of benzene from gasoline where the regional flow is the same for each soil (no biodecay in the source zone).
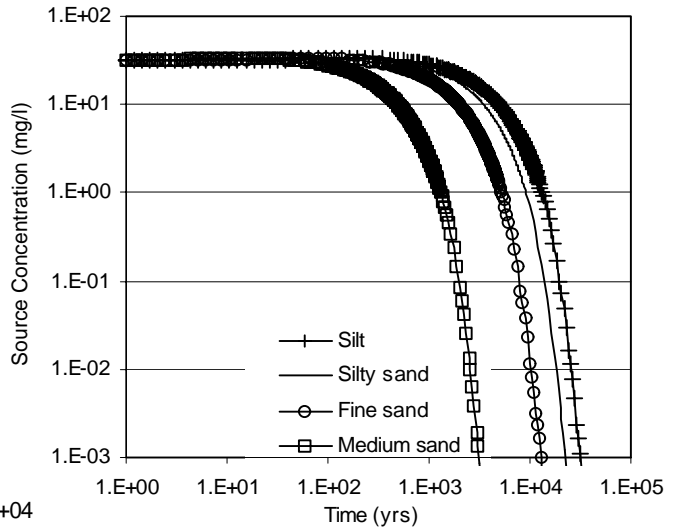
Figure E-2b. Source depletion of benzene from gasoline where the hydraulic gradient is the same for each soil (no biodecay in the source zone).

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).
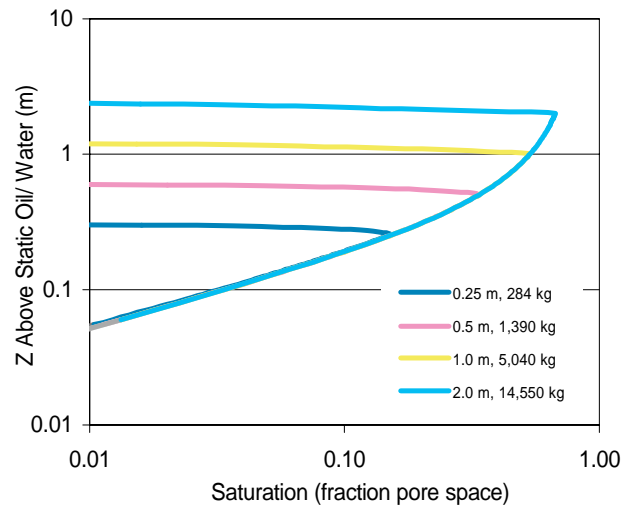

Figure E-3. Equilibrium gasoline profiles at various well thicknesses, plotted log-log to expand scale.

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.

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

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).

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%.

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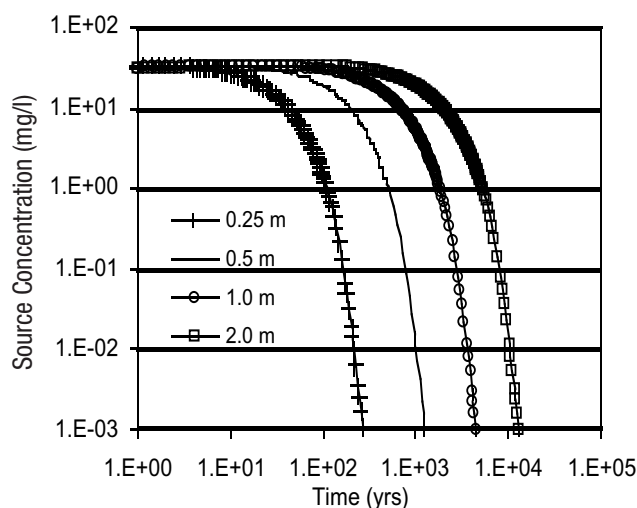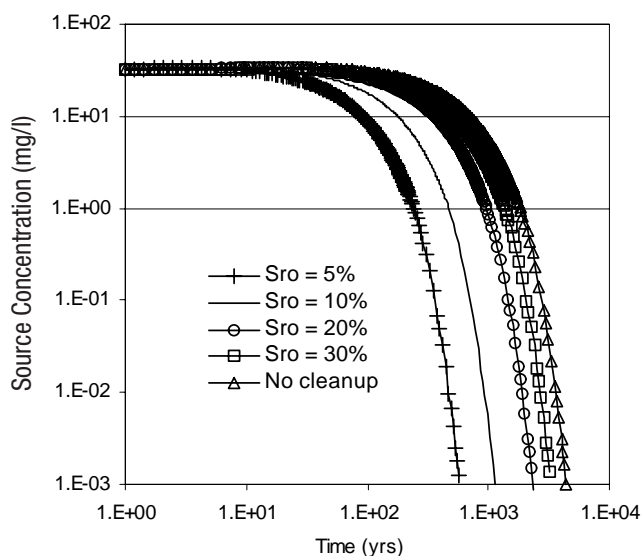
This is not to say that component losses in the vadose zone are not significant as the LNAPL spill migrates downward to the water table region, particularly for volatile compounds like MTBE.

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
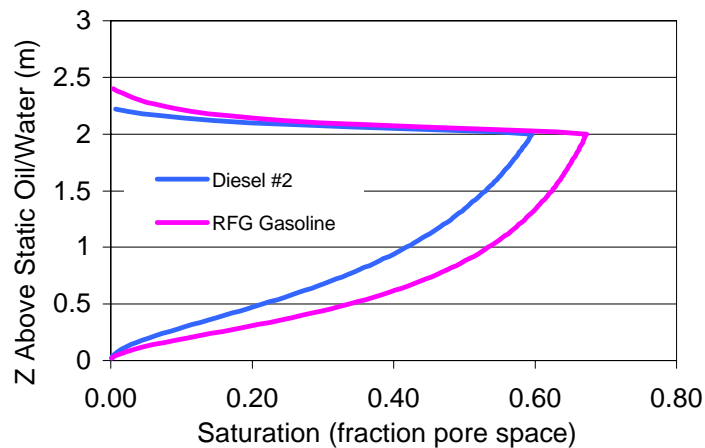

Figure E-6. Saturation profiles for 2 m observed fuel thickness, gasoline and diesel, in a fine-sand.
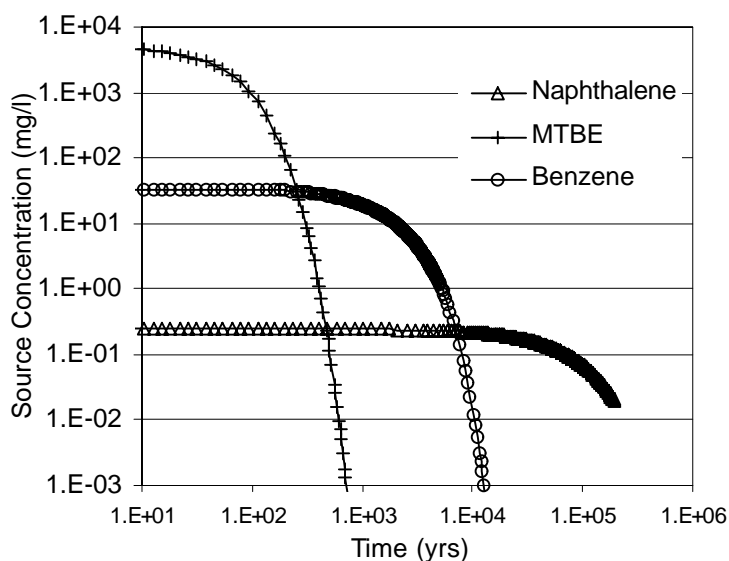

Figure E-7. Comparison of different fuel components and their longevity in the source under ambient conditions.
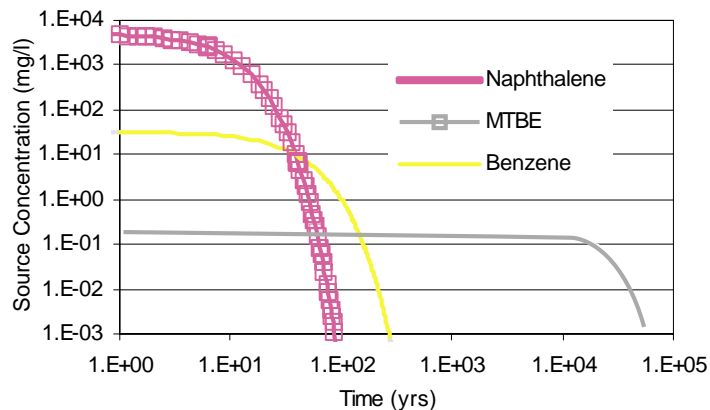

Figure E-8. The estimated source depletion graph for MTBE, benzene, and naphthalene allowing free volatilization from the source.

ES-6

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.
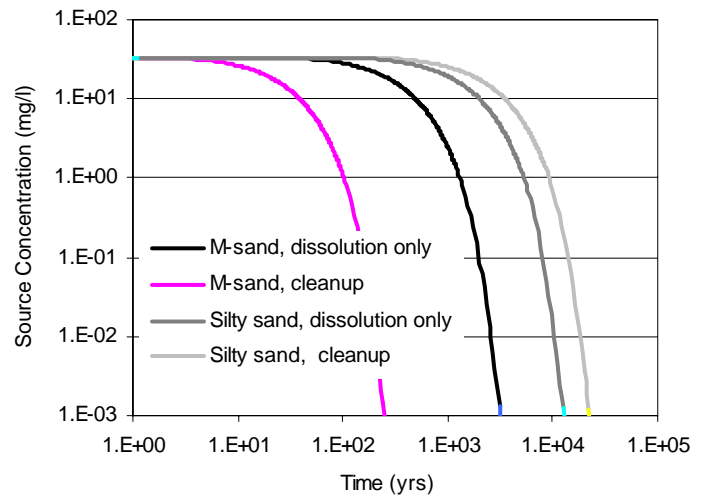

Figure E-9. Comparison of hydraulic LNAPL recovery cleanup versus intitial conditions for a silty sand and a medium sand.
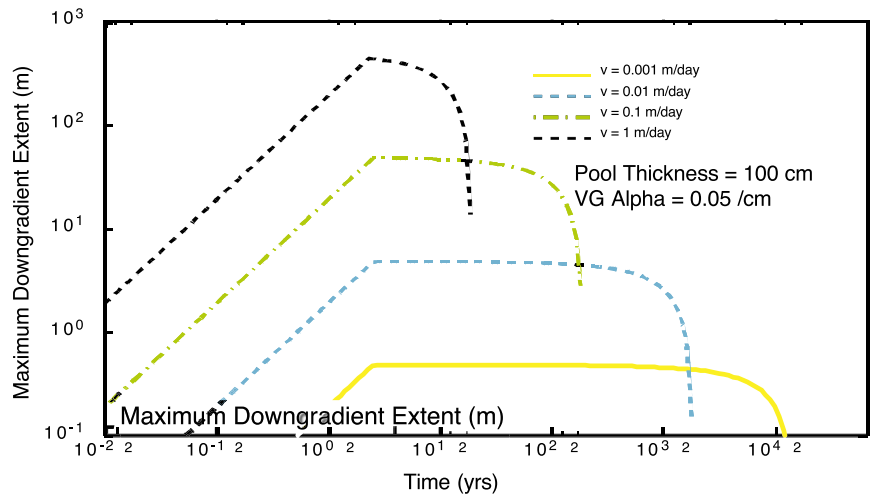
Figure E-10. The effect of groundwater velocity on the downgradient extent of benzene at a uniform decay rate.

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 dimishment 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

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, <u>at vertical equilibrium</u>, 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.