ASSESSMENT GUIDANCE FOR SITES WITH RESIDUAL WEATHERED PRODUCT

Wisconsin Department of Commerce
&
Wisconsin Department of Natural Resources

PUB-RR-787 February 2008

Purpose: This publication has been jointly developed and adopted by the Department of Commerce and the Department of Natural Resources. The purpose of this publication is to provide a technical tool for agency staff in assessing the environmental impacts of weathered petroleum product, i.e. weathered light non-aqueous phase liquids (LNAPL). This document is not intended to be used for assessing other contaminants, for assessing dissolved contaminant plume behavior, for assessing recent LNAPL releases or for determining remedial actions.

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INTRODUCTION

The intent of this document is to identify sites that have a potential for effective weathered product [i.e., light non-aqueous phase liquid (LNAPL)] remediation versus those for which a remedy will not likely be effective or necessary. The process uses a tiered approach that is focused on estimating the mobility of the remaining weathered LNAPL, determining the apparent dissolved phase plume dynamic, and assessing whether threatened or impacted receptors are present.

Active treatment (excavation and monitoring for natural attenuation not included) remedies shall be considered technically effective when a significant proportion of the LNAPL in-place can be removed. Remedies deemed likely to be ineffective shall not be approved. Excavation treatments in many cases (but not all) can be considered technically effective, however, they should also be judged on groundwater concentrations and how much of the overall contaminant mass can be effectively removed. The need for an active remedy shall be judged on site-specific LNAPL plume characteristics, dissolved plume conditions and the presence of any threatened receptors.

As one progresses through the LNAPL assessment process provided herein, approvals to proceed will be provided, if the data continue to indicate an effective remedy is possible (i.e., a significant proportion of the LNAPL is mobile and can be effectively removed). This process does not predicate a decision based on requiring that “some” remedy be conducted and then assess results, rather it uses a technically based approach to determine if recovery will likely be meaningful or beneficial.

The process provided herein focuses on historical releases. Once LNAPL has been released from a tank system, it is subject to degradation processes, and once it has reached the aquifer smear zone it is subject to the physical properties associated with dual-phase flow through a porous media. At current PECFA sites the historical LNAPL release often occurred a decade or more earlier, and it can reach an equilibrium regarding further LNAPL migration and/or contaminant loading to the groundwater. For migration, a proportion (sometimes significant) of the weathered LNAPL is not “free” or readily mobile. Rather, since most aquifers are water wet and the LNAPL is a separate phase, it is retained in the center of the soil pore spaces surrounded by groundwater. The weathered LNAPL becomes progressively less mobile as the LNAPL saturation decreases until such point that it is virtually immobile (i.e., the irreducible LNAPL saturation). For contaminant loading, natural attenuation may be shown to be sufficient to offset the contaminant flux from the weathered LNAPL. In this regard, weathered LNAPL may be no more of a risk than contaminated soil. By virtue of its simple presence, weathered LNAPL does not render the groundwater contaminant plume unstable. The remedial decisions provided herein are not intended to address recent LNAPL releases, which still likely contain a large proportion of mobile LNAPL (i.e., still being driven by a significant LNAPL head).

This document deals primarily with soil sites. Due to the wide range of bedrock situations and the limitations and issues those sites may present, professional judgment will play prominently in determining how to proceed with further testing, if at all. In the case of sandstone aquifers, some or all of the processes indicated herein may likely provide useful information to characterize weathered LNAPL flow and help determine remedial objectives. How to proceed will need to be determined on a site-by-site basis via joint DNR-Commerce decision making process.

The presence of LNAPL in a monitoring well is not itself a reliable indicator of LNAPL mobility or recoverability. Typically, the apparent LNAPL thickness in a monitoring well itself overstates the thickness of LNAPL in the native soil, and the degree of the overstatement increases with finer grained soils (Appendix B). Apparent LNAPL well thickness is also strongly influenced by water level fluctuations over time, so the timing of any particular measurement event is a factor. Simply put, LNAPL mobility cannot be determined based on the type of monitoring data that has been customarily collected to-date. LNAPL mobility can only be determined by estimating the flow (conductivity) of the LNAPL in the subject soil or bedrock. LNAPL conductivity through a porous media is dependent on the degree of LNAPL saturation and the heterogeneity of the media. In turn, LNAPL saturations are driven by the aquifer soil matrix (texture and distribution), capillary parameters, and the LNAPL fluid properties. LNAPL saturations will also be affected temporally by changes in water levels. The lateral extent of LNAPL migration is affected by conductivity, but more importantly, it is affected by the degree of the LNAPL head that originally drove it through the soil and along the aquifer smear zone. In many cases the current LNAPL head is significantly diminished or nearly non-existent (e.g., discontinuous phase LNAPL). This diminished force together with typical natural groundwater hydraulic gradients in most cases cannot overcome the inherent “retaining” capillary forces, thus limiting the weathered LNAPL’s ability to migrate laterally on a forward basis.

The process acknowledges the wide spectrum of risk that residual weathered LNAPL represents. The data collected can strongly influence the remedy selection and design stages of work. LNAPL remediation techniques and selection (including assessments of existing LNAPL treatment systems) are not part of this document.

INITIAL LNAPL ASSESSMENT PARAMETERS

The following assessment parameters shall be determined for all sites when weathered free product is present. In the case of some remedies, through DNR and Commerce concurrence, the need for one or more of the LNAPL parameters listed below may be excluded.

1. Define the lateral extent of the LNAPL and dissolved phase contaminant plumes. The estimated extent of a LNAPL plume is primarily determined by using monitoring well data (i.e., measurable free product on the water table, not soil sample results from the smear zone that exceeds NR 746.06 Table 1 values. For some sites, this may require that additional wells be installed in the source area.
    - Soil sample results from the smear zone that exceed NR 746.06 Table 1 values could be used in conjunction with monitoring well results as secondary evidence. However, soil results may be biased due to some of the practical limitations discussed below. Consequently, smear zone soil analytical results should only be used subjectively to help guide the estimate of LNAPL extent.
    - Table 1 values are not an equivalency to LNAPL in every situation. The table values are based on respective mole fractions in fresh gasoline. With weathering, the table values for the less volatile compounds become overstated, since the relative mole fraction of these compounds tends to increase as LNAPL weathers. Also, the mole fractions used for the table values are not applicable to non-gasoline sources. These effects are of particular importance when results that exceed the table values are limited to one or more of the less volatile and less soluble compounds. For example, xylenes or naphthalene.
    - Organic carbon content, which can be elevated in shallow, fine-grained soils, and organic clay or peat layers, mitigates the usefulness of the table values. Soil results can far exceed the table values with no LNAPL present. Carbon acts as a contaminant sink.
    - Matrix interference effects associated with contaminated groundwater in the source area will bias smear zone soil results.
2. Determine through quantitative lab analysis the soil type(s) across the smear zone. Qualitative boring log observations are not likely adequate; often the percentage of “fines” (silt and clay) cannot be accurately estimated. Quantitative sieve testing is needed.
    - This will likely require additional soil borings since this typically was not conducted during the investigation.
    - Important parameter for LNAPL volume calculations (see #3 below). Utilize a sieve analysis appropriate to your soil conditions. A simple “#200 screen” analysis may not be adequate if a significant proportion of the soil is clay or silt (see Appendix C for how soil results will be used).
3. Calculate the volume of LNAPL present. Use the soil type together with the greatest observed well apparent thickness to determine a Specific Volume factor (ft) that can then be multiplied by the estimated LNAPL area (ft^2) (see Appendix C). In the case of multiple wells and/or varied soil types, the LNAPL volume may need to be assessed in subdivisions.

- This estimate shall be re-evaluated when additional data, if determined to be necessary, is collected and actual thickness and actual pore space saturations are determined (e.g., undisturbed core sample analytical results).
- In general, anecdotal data (reported leak volumes) should be considered less reliable, but may be compared to the calculated volumes.

4. Collect samples of LNAPL from the monitoring wells for quantitative laboratory fluid analyses (density, viscosity, and surface and interfacial tension parameters).
    - Assess the degree of weathering by comparing to un-weathered default values.
    - Correct data to near aquifer temperature.
5. Determine apparent dissolved phase groundwater plume dynamic and whether any additional potential risks are present (e.g., proximity to drinking water wells).
    - Results from the plume margin [NR 726.05(2)(b)3], centerline and source area wells should be examined. Emphasis should be placed on long-term trends throughout the plume and short-term variation, particularly in the source area should be de-emphasized. The degree of groundwater flow divergence, both horizontal and vertical, should be considered. Conduct additional sampling or install additional wells as necessary.
    - Groundwater samples from the monitoring wells with LNAPL should also be collected. Due to the inherent variability of this sampling, the results are not intended to be used for trend analyses, but rather as a qualitative indicator of contaminant partitioning to groundwater and the overall maturity of the plume. The DNR has suggested using low-flow sampling techniques with the intake placed no more than 12 inches below the depth of the actual water table. No obvious free product should be included in the sample.
    - For historical releases, the simple presence of LNAPL does not necessarily constitute an unstable groundwater plume dynamic.
    - For the purposes of this document, an apparent plume dynamic should be determined based on the preponderance of data, not on unanimity of results (i.e., all wells and all analytes). Nearby receptors may cause a more conservative interpretation. It is acknowledged that long-term trend confirmation will be required for closure.
6. Collect coincident apparent LNAPL thickness and water level data, and evaluate for a correlation. Perform concurrent passive abatement activities, but do not use in-well absorbents since apparent thickness data may be difficult to measure. This shall not be considered a technically effective remedy.
    - Apparent LNAPL thickness variation can often be correlated to changes in water level. It is common to have LNAPL "appear" with declining or low water levels. This can in part be attributed to a drainage effect (natural difference in irreducible LNAPL saturations between the vadose and saturated zones), and is typically not an indication of recent lateral migration of the weathered LNAPL. Likewise, it is also common to have LNAPL "disappear" with rising or elevated water levels. This can in part be attributed to an imbibition effect within the newly re-saturated zone, not an indication of passive abatement success or a passing "slug" of weathered LNAPL. In

both cases (drainage and imbibition effects) the LNAPL in the monitoring well appears ephemeral, yet it is (and has been) continually present across the smear zone. Other factors that affect apparent LNAPL well thickness under dynamic water level conditions include relative LNAPL and water conductivities in the native soils and the relative hydraulic conductivity of the filter pack, which may act as a local vertical conduit to flow. However, it should not be assumed that the sudden appearance of LNAPL is due to ephemeral conditions.   LNAPL characteristics should always be observed and assessed for the potential of a new release or lateral migration.

- In the absence of a significant LNAPL head, continued lateral migration of LNAPL is unlikely. Typically, the "retaining" capillary forces are far greater than the natural horizontal groundwater flow gradients. Significant LNAPL heads can develop during the tank release event, but dissipate once the source has been eliminated. Residual LNAPL in the vadose zone source area under tension does not provide a driving head for lateral LNAPL migration along the smear zone.
- A continuous phase (higher saturations) LNAPL plume is more likely to show LNAPL presence in monitoring wells most or all of the time (Appendix D), although water level changes will still cause significant variation. Ephemeral conditions suggest near discontinuous phase (lower) saturations. LNAPL that is not present, as a continuous phase will tend to be immobile under typical groundwater flow and artificial pumping conditions.

EVALUATION OF INITIAL LNAPL ASSESSMENT PARAMETERS

Data from the six initial LNAPL assessment parameters will help to determine the appropriate response to an LNAPL plume. Additional testing, which includes the collection and analysis of undisturbed core samples, can provide site-specific inputs for LNAPL recovery models.

The three assessment parameters that appear to have the greatest effect on LNAPL hydraulic recovery are listed in the table below. Based on model sensitivity testing (Appendix E), soil type appears to have the greatest effect on treatment recovery efficiencies (i.e., *relative* LNAPL mobility), so it is a primary factor to consider when reviewing the assessment results. *Relative* LNAPL mobility as used in this document is simply a comparative recovery efficiency value estimated from model results for flow under an artificial (pump induced) gradient, not a measure of absolute mobility either induced or natural.

	Increasing Potential for LNAPL Recovery /Mobility →		
Soil Type	Predominantly clay or silt	Mixture of fine- and coarse-grained	Predominantly sand or gravel
LNAPL Fluid Properties	High density/high viscosity		Low density/low viscosity
Apparent LNAPL Thickness	Ephemeral		Continuous

The evaluation process starts with soil type. If soil types vary significantly across the LNAPL smear zone, professional judgment should be used to determine the most appropriate soil type. Assuming a predominately homogeneous soil type across the LNAPL smear zone and no nearby/impacted receptor issues, the following describes the evaluation process:

If the soil type is predominantly clay or silt then no additional recovery feasibility testing is warranted. For the purposes of this document, this also includes sand mixtures containing 40% or more fine-grained constituents (clay loams, silt loams, loams, sandy clays, and some sandy-clay loams and sandy loams). LNAPL recovery model sensitivity results using default and database values indicate a precipitous decline in recovery efficiencies for these soils when compared to more optimal sand conditions. A significant drop in recovery efficiency appears to begin in sandy soils that contain only approximately 20-30% fines. The sensitivity results for soil type (Appendix E) reflect holding all other recovery parameters at optimal values. Consequently, the efficiency declines shown will be compounded by effects due to a weathered product, less thickness of product, and/or poorly sorted sands.

If the soil contains 20-40% fines (e.g., loamy sand, some sandy loams, or some sandy-clay loams), and neither the LNAPL fluid properties nor the apparent thickness suggest high recovery potential, then no further recovery feasibility testing is warranted. Model sensitivity results using default values indicate a reduction in recovery efficiencies for highly weathered gasoline-based LNAPL. Weathered diesel and fuel oil would likely show a greater decline. Likewise, if the LNAPL is ephemeral and is significantly thinner than the sensitivity assumption, it is unlikely it is under continuous phase conditions across the smear zone, or it will become discontinuous during any hydraulic recovery attempt.

If the soil contains 20-40% fines, and either the LNAPL fluid properties or the apparent thickness suggest high recovery potential and either the groundwater plume margin appears to be expanding or a significant LNAPL volume is present, further recovery feasibility testing may be warranted.

If the soil type is predominately sand or gravel (<20% fines) and either the LNAPL fluid properties or apparent thickness suggest high recovery potential, further recovery feasibility testing is warranted. If neither the LNAPL fluid properties nor the apparent thickness data suggest high recovery potential, further recovery feasibility testing may still be warranted. If an expanding plume is suggested for the plume dynamic or a significant volume of in-place LNAPL is suggested, then further recovery feasibility testing is warranted.

The presence of nearby or impacted receptors may modify the evaluation indicated above. Assessing an excavation remedy for apparently less mobile LNAPL could be considered. For the purposes of this document, receptors are considered specific points of concern (drinking water supply wells, discharge points to surface waters or wetlands, basements, drain tiles, utility corridors, etc.). Professional judgment, which considers all the data for the site, should be employed to determine whether the additional testing will optimize remedy selection, or whether an excavation remedy is warranted, based on the currently available data. The assessment parameters themselves along with the additional feasibility testing results can qualify the potential for further LNAPL migration (degree of an imminent threat). Additionally, these results can be used to establish credible expectations on potential remedy results (i.e., set remedial targets) and/or as inputs to the remedy selection process.

If data from the LNAPL assessment parameters already suggest a significant proportion of the in-place, LNAPL cannot be recovered via active remediation and nearby receptors are not an issue, then no further recovery feasibility testing is warranted. For these sites, additional approval of remedial actions should be limited to either an excavation remedy, if appropriate or additional groundwater monitoring to confirm the dissolved plume margin dynamic. Active treatment at such sites should only be considered for unusual circumstances (e.g., persistently expanding groundwater plume margins) or in the case of threatened/impacted receptors, as described above.

REMEDIAL TREATMENT CONSIDERATIONS

Consideration of Passive LNAPL Remediation

Passive LNAPL remediation techniques generally include hand bailing and in-well absorbents and collector canisters. After the initial LNAPL assessment phase of work, which can include passive recovery activities, additional approvals for further passive abatement shall not be considered except when conducted concurrent with routine monitoring for natural attenuation (no more frequent then quarterly).

Passive recovery is simple and overall appears deceptively inexpensive. However, the consultant must mobilize to the site for each abatement event, typically the recovery volumes are irrelevant compared to the calculated volume of in-place LNAPL, and typically because of water table fluctuations, the ephemeral LNAPL will naturally be drawn back into the native soil regardless of any passive recovery activities or not. By their nature, bailing activities and in-well absorbents/canisters only collect a nominal volume of the in-place LNAPL, and only that immediately adjacent to the well. Consequently, passive LNAPL remediation provides little to no benefit relative to the volume of LNAPL present, and shall be considered an ineffective remedy.

Consideration of Excavation Treatment

Professional judgment should be used to determine whether collecting all the initial LNAPL parameters is necessary. For example, if an excavation remedy can be presumed and is needed, collecting LNAPL fluid properties would not likely be necessary. On the other hand, simply having backhoe access should not exclusively determine whether an excavation remedy is performed. Under certain site-specific conditions, closure with LNAPL in-place may be attainable even if an excavation remedy can be performed.

To characterize the need for an excavation remedy, evaluation of some or all the initial LNAPL assessment parameters may be useful. In addition, the relative amount of overall contaminant mass that can be effectively removed should be estimated and the anticipated disposal and overburden volumes shall be determined. If it appears there is little to no potential for lateral LNAPL migration, the dissolved groundwater plume dynamics are favorable and no receptor risks are present, an evaluation of long-term monitoring in lieu of an excavation should be considered.

In most cases for LNAPL excavation remedies, excavations should be limited to only the smear zone soils beneath the vadose zone soil contamination area (i.e., not extended into areas with significant non-impacted overburden soils). Low-permeability backfill or borrow materials should be considered to minimize preferential infiltration and contaminant re-mobilization.

LNAPL excavation remedies in coarse-grained soils can be problematic and may not be technically feasible. Significant dewatering activities may be necessary, thereby effectively making the remedy an active treatment, and the excavation depth may still be limited. Sidewall caving can limit the depth and lateral extent without expensive shoring techniques.

Consideration of Active Treatment – Additional LNAPL Feasibility Testing

Active treatments that address residual LNAPL should only be approved after all the initial LNAPL assessment parameters have been evaluated. The tiered evaluation process will tend to focus additional feasibility testing toward sites with 1) permeable aquifer soils, 2) LNAPL fluid properties that indicate greater mobility, and 3) a significant, continuous-phase volume. The evaluation process up to this point has been based on a mixture of site-specific and default assumption inputs.

If appropriate, additional LNAPL feasibility testing should be conducted to further define the *relative* mobility of the LNAPL using LNAPL recovery modeling based on site-specific input parameters. For example, for sand with little to no fines, recovery efficiencies can still vary significantly depending on details of the porosity architecture, which can only be determined through core analyses. Poorly-sorted sands tend to contain a much higher percentage of immobile (irreducible) LNAPL. This significantly reduces recovery efficiencies. Irreducible LNAPL saturation can only be determined through undisturbed core analyses.

Care should be taken to apply the additional testing only to sites with initial LNAPL assessment results that suggest a reasonable expectation of efficient recovery or where risk concerning a nearby receptor warrants high-grading our understanding of the LNAPL mobility.

Undisturbed Core Sample Analyses

By collecting and analyzing undisturbed cores from the LNAPL smear zone one can obtain site-specific parameters that together with the LNAPL fluid properties allow an estimate of *relative* LNAPL mobility. The parameters are inputs to LNAPL recovery models. Resultant, site-specific recovery efficiencies can then be compared to ideal values (i.e., thick, fresh, gasoline in well-sorted sand). Note that undisturbed core collection is difficult and environmental consultants may not be familiar with preservation techniques that minimize detrimental effects. Core laboratory tests are performed over considerable time frames (weeks to months), relatively few laboratories can perform the work, and environmental consultants may not be familiar with the analytical testing methods.

The following core-derived parameters are critical recovery model inputs that allow estimates of site-specific *relative* LNAPL mobility. Professional judgment is required to determine the appropriate number of samples to collect for laboratory testing.

1. Porosity.
2. Both irreducible water and irreducible LNAPL saturations can be obtained from wetting phase capillary pressure versus saturation testing. This consists of both wetting phase displacement testing to obtain drainage curves and non-wetting phase displacement testing to obtain imbibition curves (Appendix G). The van Genuchten fitting parameters need to be estimated from the resultant curves.
3. Discrete quantitative LNAPL saturations are obtained from multiple core plugs that can be collected from the undisturbed core(s). They should be spread across the entire LNAPL smear zone. Results can be directly compared to site-specific LNAPL recovery model saturation estimates. If enough samples are collected across the entire LNAPL smear zone, the results can be used to re-calculate the LNAPL volume estimate. This would eliminate the effects of using apparent monitoring well thickness on the original calculation. Results can also be used to qualify Laser Induced Fluorescence (LIF) survey results, which are only qualitative in regards to saturation data.

Due to the cost of the capillary pressure testing indicated above, in most cases only one drainage-imbibition set of analyses will be conducted, however the number of analyses will be determined on a case by case basis. Consequently, professional judgment is critical to determine the most appropriate interval. Relative permeability versus saturation testing can also be conducted on undisturbed cores to provide additional insight concerning LNAPL mobility.

The laboratory core work can include core photographs under both natural and ultraviolet light. Drilled borings will likely use Shelby tubes to collect the undisturbed cores, and for direct push, dual tube techniques may be applicable. In the case of soils that are difficult to penetrate or bedrock, other coring techniques may be required. Internal controls will likely be needed to insure that this testing is conducted at the appropriate sites (evaluation process already discussed) and in a cost effective manner.

Laser Induced Fluorescence (LIF) Surveys

This technology utilizes product fluorescence as a means to vertically define the LNAPL smear zone. When conducted in conjunction with Cone Penetrometer (CPT) and Rapid Optimal Screening Tool (ROST) technologies, it provides an indication of the vertical heterogeneity of the soils across the smear zone and a qualitative indication of LNAPL saturation, respectively. Using multiple borings during the survey one can better define the horizontal extent of the LNAPL. The LIF/ROST results are only qualitative, and do not provide parameter inputs to the LNAPL recovery models. However, once actual saturation data are available (undisturbed core analyses), the LIF/ROST results can be better qualified.

LNAPL Baildown and Pump Testing

If a sufficient thickness of LNAPL is present and the soils are permeable (reasonable recovery time), a “LNAPL only” baildown and/or pump test may be attempted. However, conducting such tests, especially recording the product and water level data concurrently, is technically difficult and should not be considered unless permeable soils and a significant thickness of product is present. Modified (from groundwater) analyses can then be performed on the recovery curve to provide an estimate of the LNAPL conductivity. The conductivity can be used as an input to LNAPL recovery models for the design phase of active treatment systems.

REFERENCES

American Petroleum Institute (API), May 2003, *Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites*, API Soil and Groundwater Research Bulletin Number 18.

Charbeneau, R. J., R. T. Johns, L. W. Lake, and M. J. McAdams, June 1999, *Free-Product Recovery of Petroleum Hydrocarbon Liquids*, API Publication Number 4682.

Remediation Technologies Development Forum (RTDF), February 2005, *Understanding the Behavior of Light Non-Aqueous Phase Liquids (LNAPLs) in the Subsurface*, PowerPoint Slides.

APPENDICES

Appendix A

Case Closure with Residual Free Product
December 2002 RE NEWS (DNR Pub-RR-703)
p. 1-3

Appendix B

LNAPL in a Well and Adjacent Formation
Slide 18 (RTDF, 2005)

Appendix C

Specific Volume vs. Monitoring Well Thickness
Slide 24 (RTDF, 2005)

Appendix D

Effect of Thickness in Monitoring Well on Saturation in Silty Sand
Slide 22 (RTDF, 2005)

Appendix E

Weathered LNAPL Recovery Model Sensitivity Testing Results

Appendix F

Drainage and Imbibition Capillary Pressure Curves
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Information from Wisconsin Department of Natural Resources Bureau for Remediation and Redevelopment

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FEATURE

Case Closure With Residual Free Product- Can You Get There From Here?

Yes. But there are no shortcuts. The following article is a summary of essential tech components of any request for case closure at a contaminated site that still has som ual petroleum free product.

The Remediation and Redevelopment (RR) Program uses teams to develop many of the procedures and guidance documents that are important to environmental cleanup and redevelopment of contaminated properties. One such team, the NR 700 Implementation Team, is charged with assisting RR staff in the consistent application of the NR 700 rule series. Each of the DNR's five regions has a member on this team.

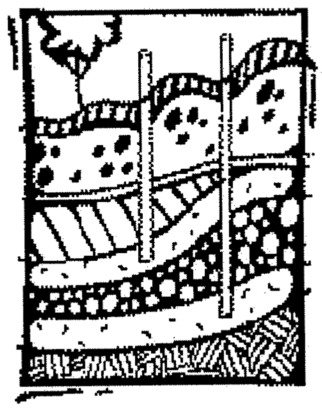
Program staff also frequently meet with different stakeholder groups working on investigation and cleanup of contaminated sites, seeking input on RR programs and policies. One such group, the NR 700 Consultants Focus Group, is composed of private environmental consultants who meet quarterly with RR staff to discuss technical items of mutual interest.

About a year ago, the Consultants Focus Group asked the RR Program about the possibilities for case closure at sites

Case Closure With Residual Free Product - Can You Get There From Here? (con't.)

with residual free product consisting of petroleum. Normally, sites that are approved for closure with any remaining contamination are those sites with petroleum contamination in the groundwater where natural attenuation is working to slowly reduce the amount of contamination.

Petroleum "free product", however, is any petroleum contamination that exists as a separate, floating material that does not readily mix with or dissolve in water. Consultants were wondering: Could some sites be closed if residual, petroleum free product is present?



The consultant's question was given to the NR 700 Implementation Team. Team members had several discussions regarding NR 700 rule requirements that apply to different types of sites with residual free product, and over the course of a year defined the issues that arise when considering case closure at these sites.

In August, 2002, the NR 700 Implementation Team met with the Consultants Focus Group to discuss the primary factors that RR regional case closure committees evaluate when considering case closure with residual petroleum product. The most important concepts from that discussion are summarized here.

1. Does the presence of residual free product prohibit case closure?

No. The NR 700 Implementation Team estimated that about a dozen sites with residual free product are closed by DNR each year.

2. What specific regulations apply to sites with residual free product?

Section NR 708.13, Wis. Adm. Code, which is based on the requirements in the Code of Federal Regulations (40 CFR 280.64), states: "Responsible parties shall conduct free product removal whenever it is necessary to halt or contain the discharge of a hazardous substance or to minimize the harmful effects of the discharge to the air, lands or waters of the state."

In the past, RR staff usually interpreted this to mean that free product causes a continuous discharge and must be "halted" by its removal. More recently, however, after looking at the volume of product already removed as well as the estimated volume of product remaining, the RR Program is also considering other factors. These are:

- the technical feasibility of continued free product removal as evaluated under ss. NR 722.07 and 722.09 (identification and selection of remedial actions), Wis. Adm. Code; and
- the likelihood of continuing discharges of dissolved contaminants into groundwater from weathered free product.

In general, RR Program staff considering case closure will first look at prior efforts to remove free product, and then look at the volume of product remaining, the degree of weathering, and groundwater monitoring to evaluate whether there is an ongoing discharge of dissolved contaminants to groundwater. If there is an ongoing discharge to groundwater from the remaining free product, further remedial actions will be needed.

3. How can consultants estimate the extent of free product without significantly increasing the number of monitoring wells?

The DNR advises that the following guidelines may be helpful:

- Collect soil samples from the soil/groundwater interface (termed the "smear zone") to estimate the horizontal and vertical extent of free product. Compare the analytical results from these samples to the values in Table 1 of s. NR 746.06, Wis. Adm. Code. These table values were developed as approximations of soil saturation levels and reflect the likelihood of finding free product on the water table. Use these samples to delineate or map the free product plume. Quarterly groundwater samples in the source area should be used to approximate the depth of free product on the water table, and the seasonal variability in water table elevations.

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- Don't be in a rush. Long-term monitoring is a critical component in evaluating the impact of the residual product on groundwater quality. Allow time for the effects of groundwater level fluctuations to become apparent. These are not going to be fast closures.

4. How can consultants get DNR input prior to submitting a case closure request?

For a fee of $500, consultants should take advantage of the RR Program's technical assistance to get a written opinion, detailed verbal comments or to hold a technical meeting to discuss your site. You can use this assistance to better understand DNR's position on the feasibility of free product remediation or recovery options prior to submitting a closure request.

5. Where can I find a discussion of technical considerations regarding free product and case closure with natural attenuation?

Publication #RR-614, Guidance On Natural Attenuation For Petroleum Releases includes several discussions regarding free product. This publication is available on the RR Program web site at www.dnr.state.wi.us/org/aw/rr, using the "Publications" button in the lower left corner of the page. The following topics are covered on the pages listed:

- Page 9 – cleanup to the extent practical;
- Page 13 – identifying the degree and extent of contamination;
- Page 23 – free product removal before evaluating natural attenuation as a remedy;
- Page 24 – mapping the extent of free product;
- Page 27 – how free product affects the calculation of the decay rate;
- Pages 37-39 – requirements for case closure; and
- Page 43 – removal of free product to the extent practicable as required under s. NR 722.09(2) and s. NR 726.05 (2)(b)(1)(e), Wis. Adm. Code.

In Appendix A1:
- Page 13 – phases of contamination and calculation of contaminant mass;
- Page 65 – references for calculating mass of product when a sheen remains;
- Page 67 – delineation of free product in the saturated source zone; and
- Page 78 – estimating contaminant decay affected by the age of free product.

6. What can consultants do to ensure consideration when submitting a case closure request with residual free product?

- Estimate the total volume of free product remaining in the environment. The NR 700 Implementation Team has noted that this step is rarely done by consultants, and is an important consideration in the case closure request.

- Clearly summarize what recovery and/or remedial action efforts have been undertaken to recover free product. Members of the NR 700 Implementation Team estimated that at least half of all case closure requests with residual petroleum free product have not included a discussion on remedial actions that have been taken to address the free product.

- Clearly list and discuss the range of alternatives for recovering or remediating the remaining free product. In the discussion, summarize the technical feasibility and estimated cost of each alternative relative to site-specific conditions (e.g. hydrogeology, risk, and accessibility of product). This helps technical staff and regional closure committees evaluate the level of effort that has been made in relation to the range of alternatives.

Contact Information for the NR 700 Implementation Team and Consultants Focus Group

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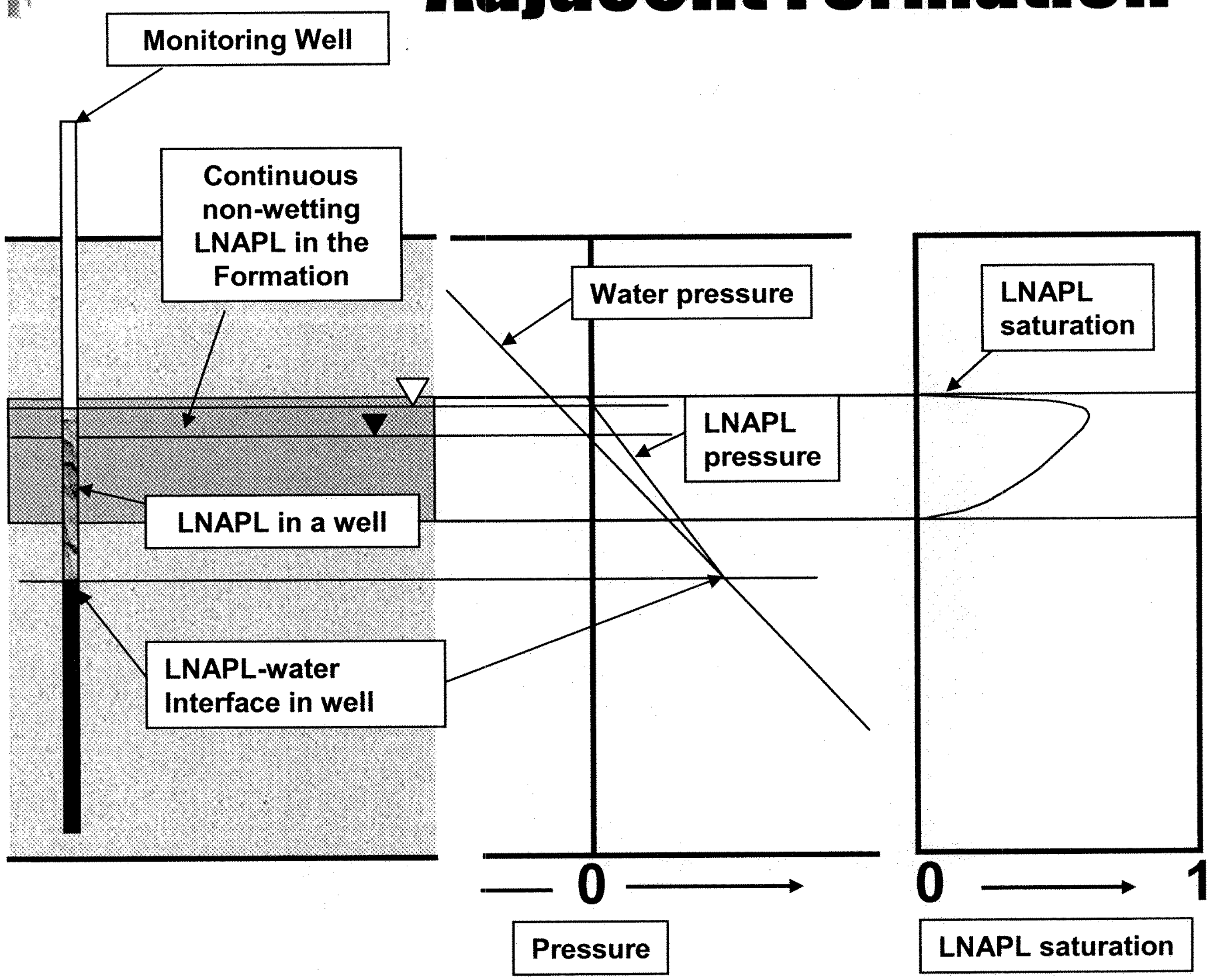
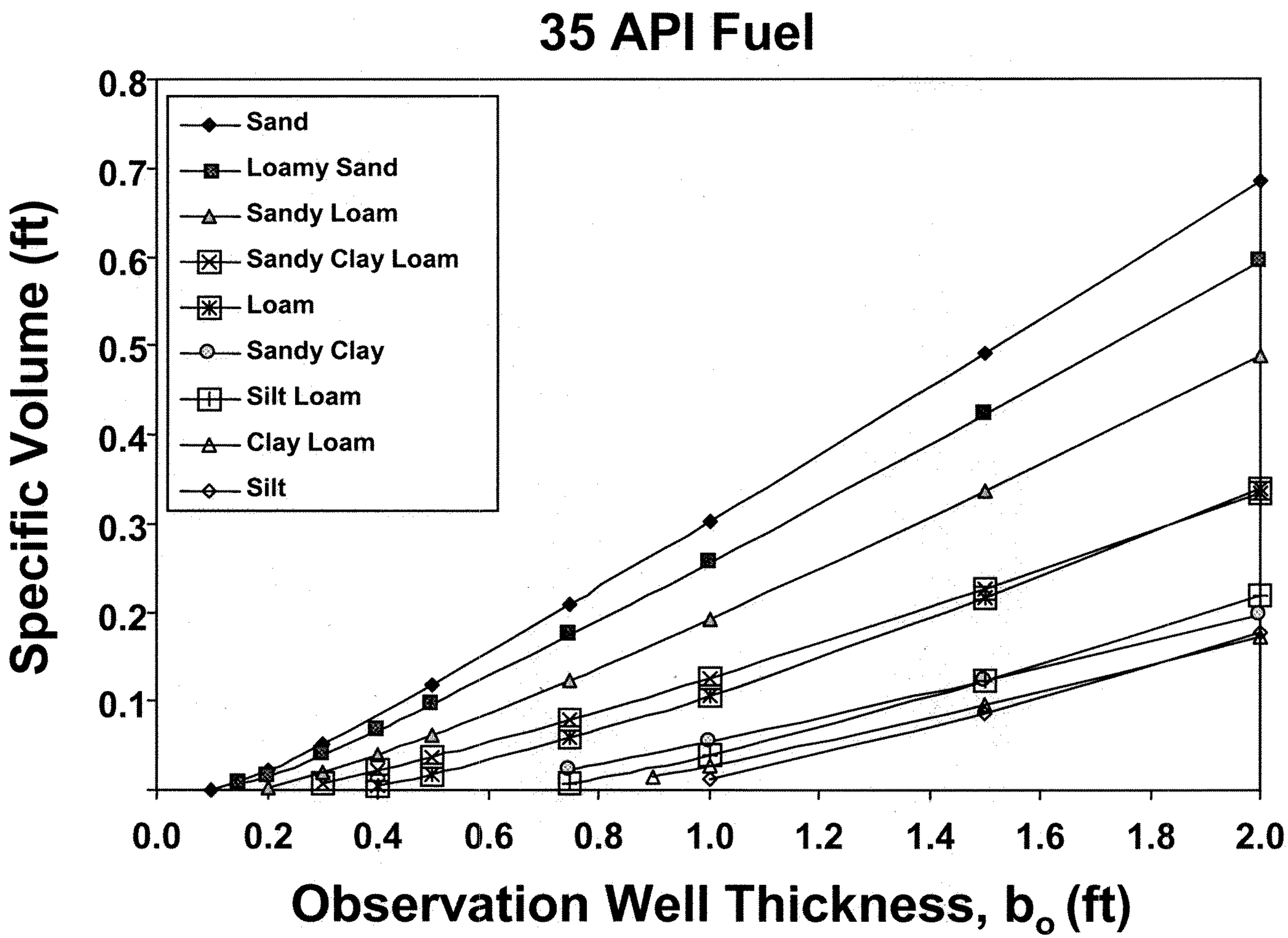
RTDF

LNAPL in a Well and Adjacent Formation

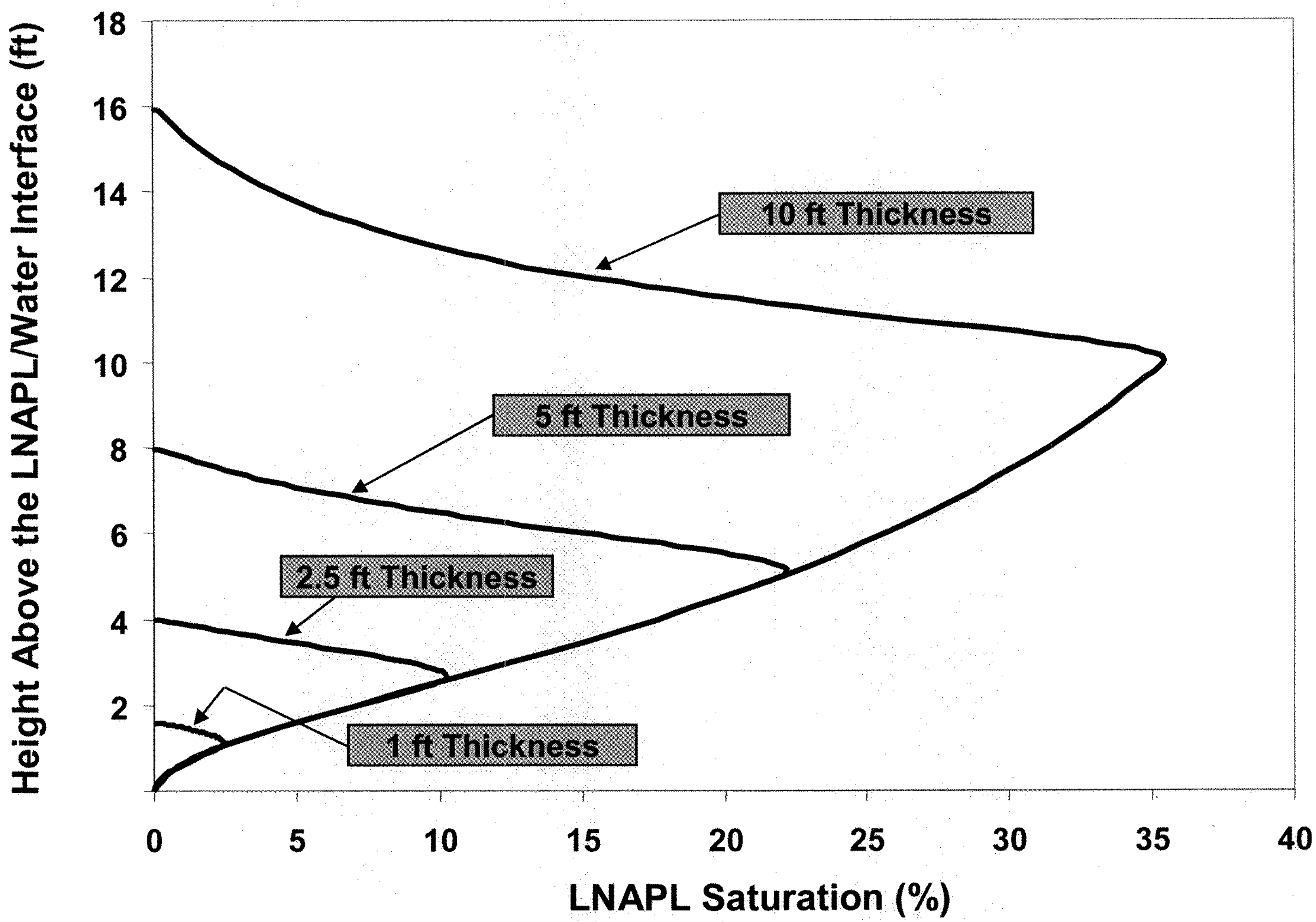


Specific Volume vs. Monitoring Well Thickness



RTDF

Effect of Thickness in Monitoring Well on Saturation in Silty Sand



Appendix E - Weathered LNAPL Recovery Model Sensitivity Testing Results

API van Genuchten-Burdine Model of LNAPL Distribution and Realtive Permeability (Single Layer)[1]

Skimmer well Q_w = 0, t = 2yr, R_c = 20ft

Soil Type Sensitivity Testing

Input Constants (from API LNAPL model reference worksheets):

LNAPL thickness (ft)	b_o	3	
LNAPL density (gm/cc)	ρ_o	0.73	[un-weathered gasoline at 15^0 C]
air-water tension (dynes/cm)	σ_{aw}	65	[assumed for contaminated groundwater]
air-oil tension (dynes/cm)	σ_{aw}	21	[fresh gasoline]
oil-water tension (dynes/cm)	σ_{aw}	50	[fresh gasoline]
LNAPL viscosity at 60^0F (cP)	μ_0	0.62	[fresh gasoline (B-Vennard and Street, 1982)]

Soil Default Variables (from API LNAPL model reference worksheets):

soil types		Sand	Loamy Sand	Sandy Loam	Loam	Clay Loam
porosity	n	0.43	0.41	0.41	0.43	0.41
van Genuchten "N"	N	2.68	2.28	1.89	1.56	1.31
van Genuchten "α"	α	4.4	3.8	2.3	1.1	0.58
irreducible water saturation[2]	S_{wr}	0.1	0.14	0.16	0.18	0.23
irreducible LNAPL sat. (vadose)	S_{orv}	0.021	0.057	0.057	0.057	0.057
irreducible LNAPL sat. (sat.zone)	S_{ors}	0.12	0.17	0.19	0.22	0.27
aquifer conductivity (ft/d)	K_w	23	11	3.6	0.82	0.2
Recovery Model Results:						
in-place volume		8006	6846	5253	4402	5997
recovered volume		6551	4295	1634	97	2
recovery efficiency		82%	63%	31%	2%	0%
relative mobility (reduction from ideal sd.)		**-**	**-23%**	**-62%**	**-97%**	**-100%**
irreducible water saturation[4]	S_{wr}	0.045	0.057	0.065	0.078	0.095
in-place volume		8045	6846	5260	4405	5761
recovered volume		6273	4295	1630	97	2
recovery efficiency		78%	63%	31%	2%	0%
relative mobility[3] (reduction from ideal sd.)		-	**-20%**	**-60%**	**-97%**	**-100%**

Soil Default Variables (from API Soil Parameters Database):

% fines (quartiles)		< 11%	11-41%	41-72%	>72%
porosity	n	0.42	0.42	0.43	0.43
van Genuchten "N"	N	2.52	2.23	1.86	1.79
van Genuchten "α" (ft^{-1})	α	0.71	0.92	0.34	0.3
irreducible water saturation	S_{wr}	0.19	0.25	0.43	0.48
irreducible LNAPL sat. (vadose)	S_{orv}	0.021	0.057	0.057	0.057
irreducible LNAPL sat. (saturated z	S_{ors}	0.12	0.17	0.22	0.27
hydraulic conductivity (ft/d)	K_w	430	60	57	0.77
Recovery Model Results:					
in-place volume		2473	3421	3974	5578
recovered volume		1049	1205	45	0
recovery efficiency		42%	35%	1%	0%
relative mobility[3] (reduction from ideal sd.)		-	**-17%**	**-97%**	**-100%**

Notes:

[1] API Publication 4729, Models for Design of Free Product Recovery Systems for Petroleum Hydrocarbon Liquids (August, 2003)

[2] from API Publ. 4729 (Carbeneau, 1999)

[3] Comparative efficiency, not a measure of absolute LNAPL mobility

[4] from API Publ. 4729 (Carsell & Parish, 1988)

default data for S_{orv} is limited, 0.057 value is silt to fine sand (Mercer & Cohen, 1990)

default data for S_{ors} is limited, value for sand is lower limit (Mercer & Cohen, 1990), for soils with finer grained constiuents varied as Swr.

individual parameter plots suggest 20-30% fines as breakover to less efficient recovery

Appendix E - Weathered LNAPL Recovery Model Sensitivity Testing Results

API van Genuchten-MualemModel of LNAPL Distribution and Realtive Permeability (Single Layer)[1]
Skimmer well Q_w = 0, t = 2yr, R_c = 20ft

Soil Type Sensitivity Testing

Input Constants (from API LNAPL model reference worksheets):

LNAPL thickness (ft)	b_o	3	
LNAPL density (gm/cc)	ρ_o	0.73	[un-weathered gasoline at 15^0 C]
air-water tension (dynes/cm)	σ_{aw}	65	[assumed for contaminated groundwater]
air-oil tension (dynes/cm)	σ_{aw}	21	[fresh gasoline]
oil-water tension (dynes/cm)	σ_{aw}	50	[fresh gasoline]
LNAPL viscosity at 60^0F (cP)	μ_0	0.62	[fresh gasoline (B-Vennard and Street, 1982)]

Soil Default Variables (from API LNAPL model reference worksheets):

soil types		Sand	Loamy Sand	Sandy Loam	Loam	Clay Loam
porosity	n	0.43	0.41	0.41	0.43	0.41
van Genuchten "N"	N	2.68	2.28	1.89	1.56	1.31
van Genuchten "α"	α	4.4	3.8	2.3	1.1	0.58
irreducible water saturation[2]	S_{wr}	0.1	0.14	0.16	0.18	0.23
irreducible LNAPL sat. (vadose	S_{orv}	0.021	0.057	0.057	0.057	0.057
irreducible LNAPL sat. (sat.zon	S_{ors}	0.12	0.17	0.19	0.22	0.27
aquifer conductivity (ft/d)	K_w	23	11	3.6	0.82	0.2
Recovery Model Results:						
in-place volume		8006	7180	5253	4405	5997
recovered volume		6551	5027	2630	753	173
recovery efficiency		82%	70%	50%	17%	3%
relative mobility (reduction from ideal sd.)		**-**	**-14%**	**-39%**	**-79%**	**-96%**
irreducible water saturation[4]	S_{wr}	0.045	0.057	0.065	0.078	0.095
in-place volume		8045	7180	5260	4405	5761
recovered volume		6522	5027	2623	746	171
recovery efficiency		81%	70%	50%	17%	3%
relative mobility[3] (reduction from ideal sd.)		-	**-14%**	**-38%**	**-79%**	**-96%**

Soil Default Variables (from API Soil Parameters Database):

% fines (quartiles)		< 11%	11-41%	41-72%	>72%
porosity	n	0.42	0.42	0.43	0.43
van Genuchten "N"	N	2.52	2.23	1.86	1.79
van Genuchten "α" (ft^{-1})	α	0.71	0.92	0.34	0.3
irreducible water saturation	S_{wr}	0.19	0.25	0.43	0.48
irreducible LNAPL sat. (vadose	S_{orv}	0.021	0.057	0.057	0.057
irreducible LNAPL sat. (saturate	S_{ors}	0.12	0.17	0.22	0.27
hydraulic conductivity (ft/d)	K_w	430	60	57	0.77
Recovery Model Results:					
in-place volume		2473	3438	3992	5669
recovered volume		1166	1480	650	69
recovery efficiency		47%	43%	16%	1%
relative mobility[3] (reduction from ideal sd.)		-	**-9%**	**-65%**	**-97%**

Notes:

[1] API Publication 4729, Models for Design of Free Product Recovery Systems for Petroleum Hydrocarbon Liquids (August, 2003)

[2] from API Publ. 4729 (Carbeneau, 1999)

[3] Comparative efficiency, not a measure of absolute LNAPL mobility

[4] from API Publ. 4729 (Carsell & Parish, 1988)

default data for S_{orv} is limited, 0.057 value is silt to fine sand (Mercer & Cohen, 1990)

default data for S_{ors} is limited, value for sand is lower limit (Mercer & Cohen, 1990), for soils with finer grained constiuents varied as Swr.

individual parameter plots suggest 20-30% fines as breakover to less efficient recovery

Appendix E - Weathered LNAPL Recovery Model Sensitivity Testing Results

API van Genuchten-Burdine Model of LNAPL Distribution and Realtive Permeability (Single Layer)[1]
Skimmer well Q_w = 0, t = 2yr, R_c = 20ft

LNAPL Fluid Property Sensitivity Testing

Input Constants (from API LNAPL model reference worksheets for highly recoverable sand):

LNAPL thickness (ft)	b_o	3	
air-water tension (dynes/cm)	σ_{aw}	65	[assumed for contaminated groundwater]
porosity	n	0.43	[optimal well-sorted sand]
van Genuchten "N"	N	2.68	[optimal well-sorted sand]
van Genuchten "α" (ft^{-1})	α	4.4	[optimal well-sorted sand]
irreducible water saturation	S_{wr}	0.045	[optimal well-sorted sand]
hydraulic conductivity (ft/d)	K_w	23	[optimal well-sorted sand]

LNAPL Fluid Default Variables (from API LNAPL model reference worksheets):

fluid type		Fresh Gasoline	Weathered Product[2]
LNAPL density (gm/cc)	ρ_o	0.73	0.88
air-oil tension (dynes/cm)	σ_{aw}	21	27
oil-water tension (dynes/cm)	σ_{aw}	50	48
LNAPL viscosity at 60^oF (cP)	μ_0	0.62	2.7
irreducible LNAPL sat. (vadose)	S_{orv}	0.021	0.086
irreducible LNAPL sat. (sat.zone)	S_{ors}	0.12	0.2
Recovery Model Results:			
in-place volume		8459	6235
recovered volume		6742	2191
recovery efficiency		80%	35%
relative mobility[3] (reduction from ideal sd.)		-	**-56%**

Notes:

[1] API Publication 4729, Models for Design of Free Product Recovery Systems for Petroleum Hydrocarbon Liquids (August, 2003)

[2] Weathered product values not available, values reflect unweathered diesel or fuel oil parameters

[3] Comparative efficiency, not a measure of absolute LNAPL mobility

Appendix E - Weathered LNAPL Recovery Model Sensitivity Testing Results

API van Genuchten-Burdine Model of LNAPL Distribution and Realtive Permeability (Single Layer)[1]
Skimmer well Q_w = 0, t = 2yr, R_c = 20ft

Irreducible Oil Saturation Sensitivity Testing

Input Constants (from API LNAPL model reference worksheets for highly recoverable sand):

LNAPL thickness (ft)	b_o	3	
LNAPL density (gm/cc)	ρ_o	0.73	[un-weathered gasoline at 15^{0} C]
air-water tension (dynes/cm)	σ_{aw}	65	[assumed for contaminated groundwater]
air-oil tension (dynes/cm)	σ_{aw}	21	[fresh gasoline]
oil-water tension (dynes/cm)	σ_{aw}	50	[fresh gasoline]
LNAPL viscosity at 60^{0}F (cP)	μ_0	0.62	[fresh gasoline (B-Vennard and Street, 1982)]
porosity	n	0.43	[optimal well-sorted sand]
van Genuchten "N"	N	2.68	[optimal well-sorted sand]
van Genuchten "α" (ft^{-1})	α	4.4	[optimal well-sorted sand]
irreducible water saturation[2]	S_{wr}	0.045	[optimal well-sorted sand]
irreducible LNAPL sat. (vadose)	S_{orv}	0.021	[optimal well-sorted sand]
hydraulic conductivity (ft/d)	K_w	23	[optimal well-sorted sand]

Irreducible LNAPL Saturation Default Variable (from API LNAPL model reference worksheets):

		Well-sorted Sand	Poorly-sorted Sand
degree of sorting			
irreducible LNAPL sat. (sat.zone)	S_{ors}	0.12	0.5
<u>Recovery Model Results:</u>			
in-place volume		8459	10247
recovered volume		6742	5012
recovery efficiency		80%	49%
relative mobility[3] (reduction from ideal sd.)		**-**	**-39%**

Notes:

[1] API Publication 4729, Models for Design of Free Product Recovery Systems for Petroleum Hydrocarbon Liquids (August, 2003)

[2] from API Publ. 4729 (Carsell & Parish, 1988)

[3] Comparative efficiency, not a measure of absolute LNAPL mobility

RTDF

Drainage and Imbibition Capillary Pressure Curves