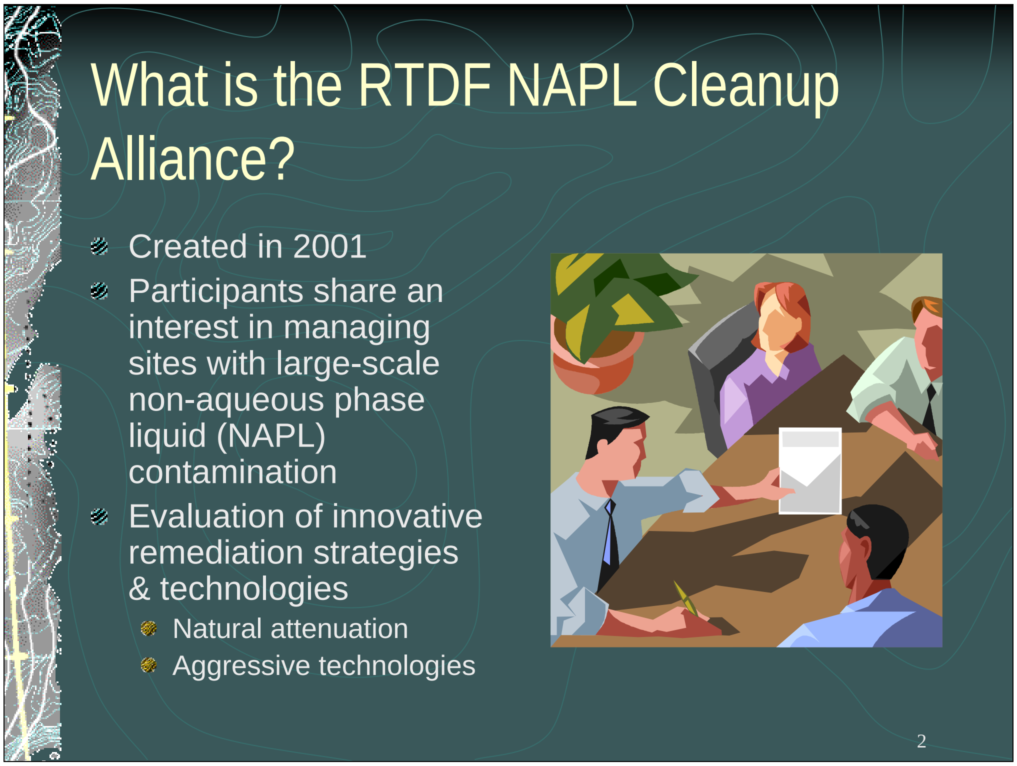
Incorporates edits from HH, JH, ER and BM provided June 2005

Edits from VJK on 10-12-05



Includes representatives from the petroleum industry, federal and state government, and academia

Provide Training in LNAPL Science

Purpose of this Presentation

- Raise awareness of how the current understanding of LNAPL behavior in the subsurface can be used in a decision framework to better manage LNAPL sites.
- Begin a dialog to improve cleanup and cleanup decision making.

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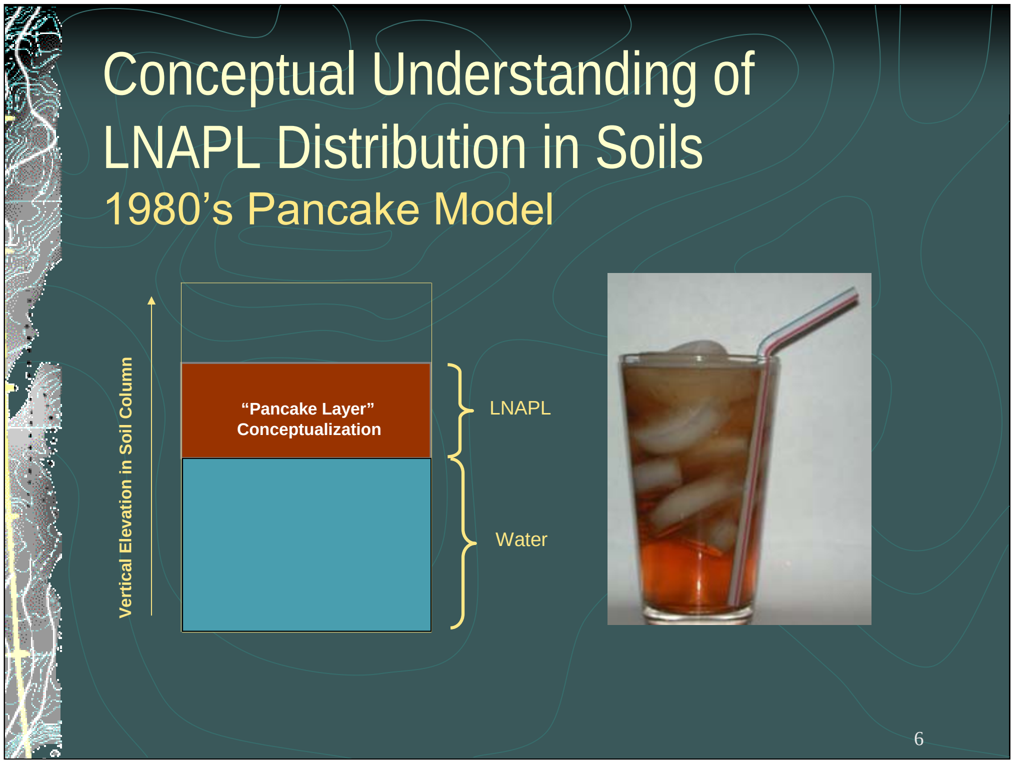
There are some parallels between how we used to address soil contamination and how it is approached today and how LNAPL is addressed today and where we see it going. As stakeholders began to recognize that not all contamination could be removed at some sites a site management approach became more accepted. Prior to managed decision making, one-size fits all values were used for cleanup. Although some states do not officially recognize risk-based decision making today, a managed approach is used to determine an appropriate cleanup level for the protection of a relevant exposure pathway. Similarly LNAPL thickness in a well may be one important observation about LNAPL bet it doesn't tell the whole story. The emerging frameworks provide a more holistic look at LNAPL.

Outline of this Presentation

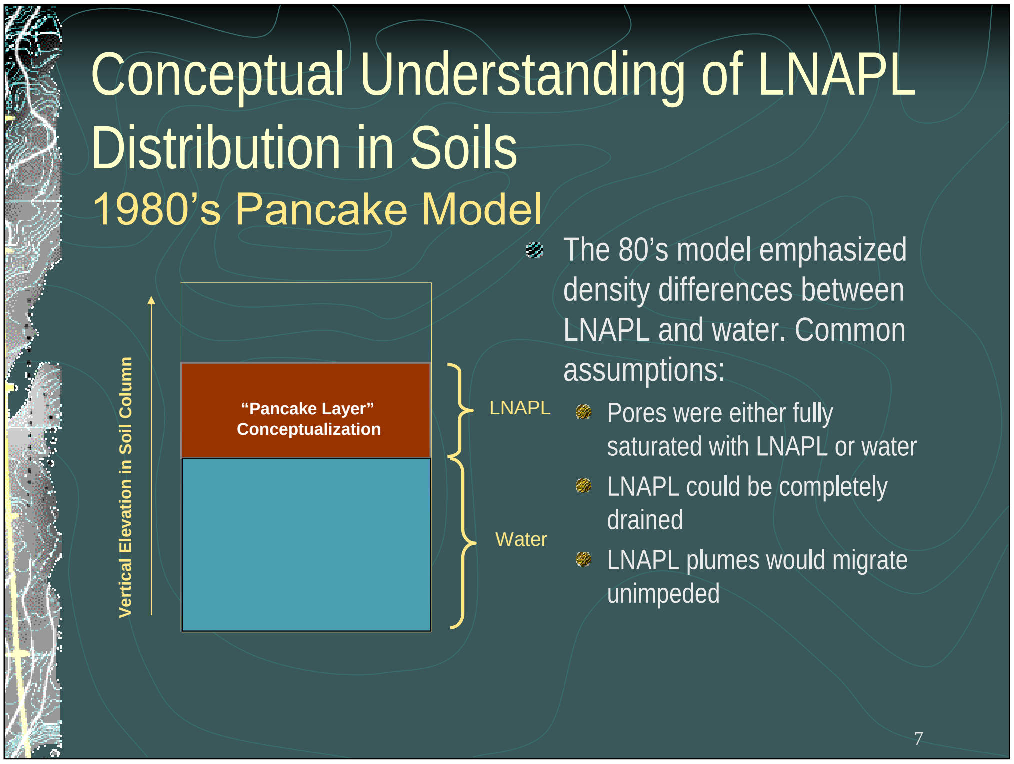
- LNAPL behavior & case study
  - Conceptual model for pore-scale LNAPL distribution
  - Mobility
  - Significance of direct observations
- RTDF Framework highlighting available tools & guides
  - ASTM
  - API Interactive LNAPL Guide



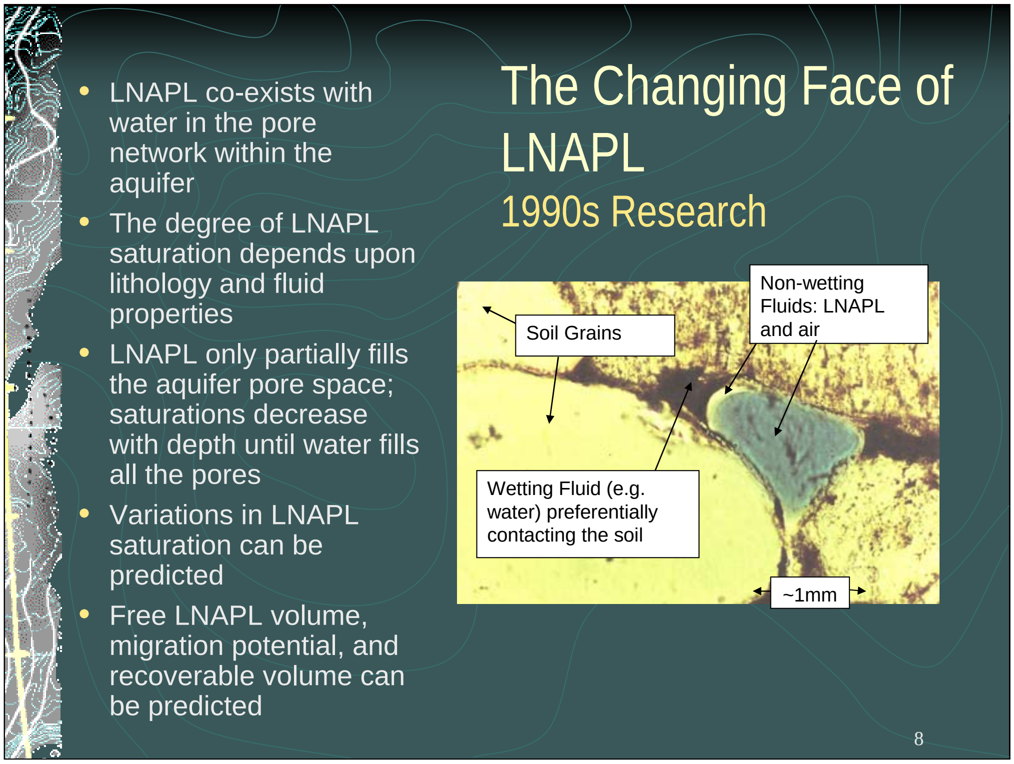
To Do:

Replace the ice tea with liquids that look more like LNAPL over water. This will more clearly illustrate fluids of different densities.

The 1980s model emphasized differences in fluid densities. This model envisioned pores fully saturated with oil floating on water. In addition to the notion that the oil could be entirely drained, this model leads to the misconception that you could completely recover LNAPL and that plumes could freely migrate. The '80s model does not recognize the complexity of pore-scale interaction with multiple fluid phases.



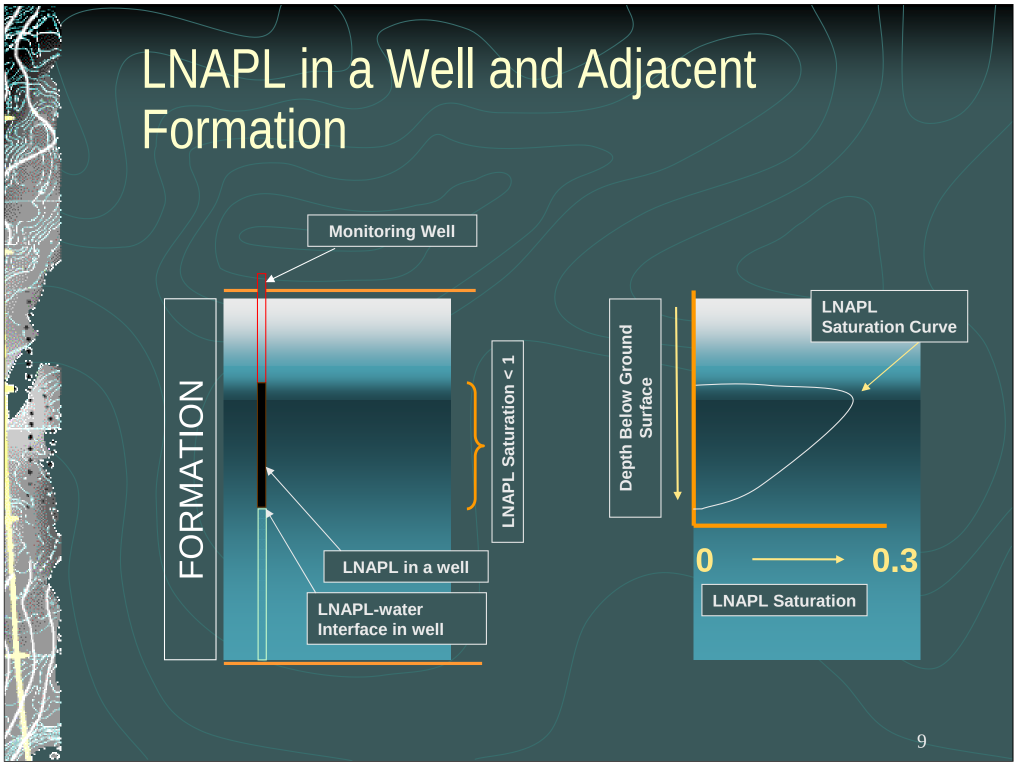
To Do: Eventually combine this slide with the previous slide thru animation



We now understand that LNAPL **co-exists with water in the pore network within the aquifer**. It does not float on the water table.

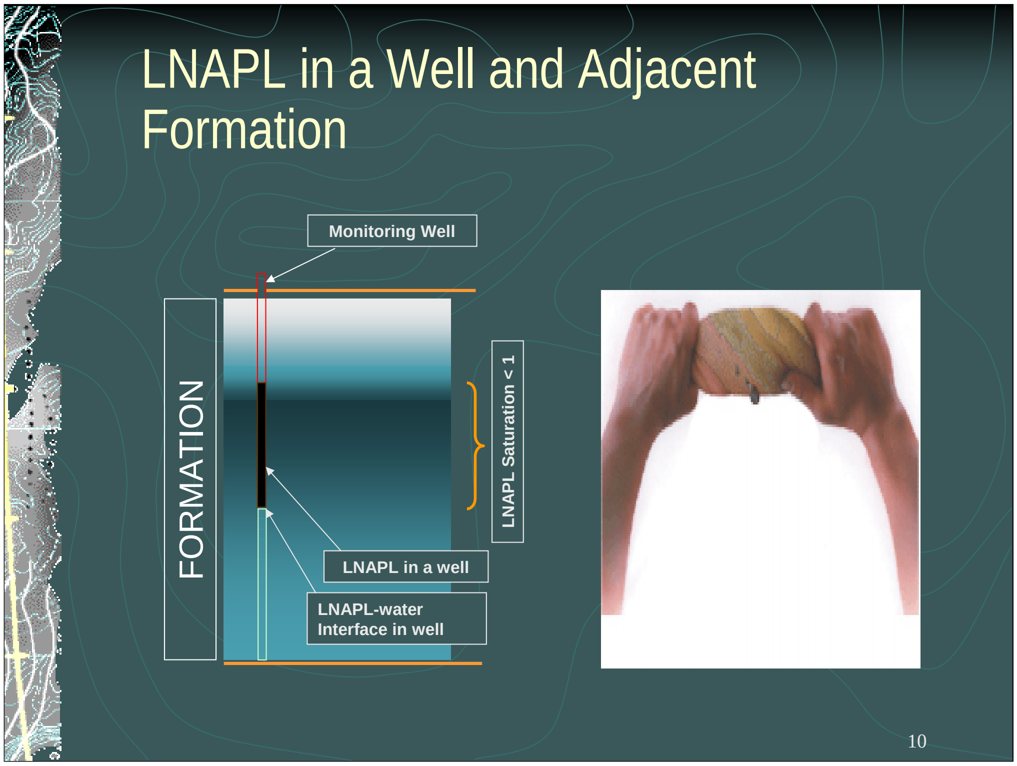
The degree of LNAPL saturation depends on the history, **lithology**, capillary parameters, and fluid properties of the site and the volume of LNAPL released. LNAPL only partially fills the aquifer pore space, and saturation decreases with depth until water fills all the pores.

The variation with depth of LNAPL saturation in the subsurface can be predicted when the properties of the subsurface media and fluid are known, and the apparent LNAPL thickness in the well is measured. This is accomplished by using the theories of Farr and McWhorter, and Lenhard and Parker. If sufficient measurements are taken across an LNAPL plume, the total volume of free LNAPL, its migration potential, and the recoverable volume also can be predicted. **Spreadsheets (API Publication 4729)** to perform these calculations have been made available by Randy Charbeneau for the API.



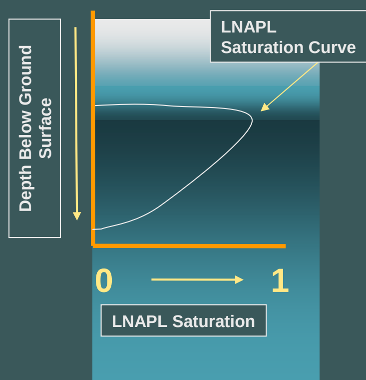
Physical properties dictate that there will be some recoverable LNAPL and some residual LNAPL left behind.

The LNAPL left behind & its chemistry defines the benefit and timing of the mitigation or management strategy.



In contrast, consider the point roller model of LNAPL distribution in the subsurface. LNAPL (paint) is drawn into the roller by capillarity. In some places in the roller, the paint saturation is high, in others the paint shares the pores with air and the water leftover the last time the roller was washed. As you know, washing the paint out is very difficult; no matter how much you rinse and squeeze, paint still comes out. Even when you lay the roller down for a while, paint still comes out

Recognizing the Significance of LNAPL Residual



Physical properties dictate that there will be some recoverable LNAPL and some residual LNAPL left behind.

The LNAPL left behind & its chemistry defines the benefit and timing of the mitigation or management strategy.

Hydraulic recovery is one

LNAPL Migration

- Affected by:
  - LNAPL Fluid Properties
  - LNAPL Relative Permeability
  - Conductivity of the Porous Media
  - Hydraulic Gradient
  - Pore Throat Displacement Entry Pressure
  - Fluctuating Water Table

At many sites, these factors combine to produce a plume that is not spreading or migrating.

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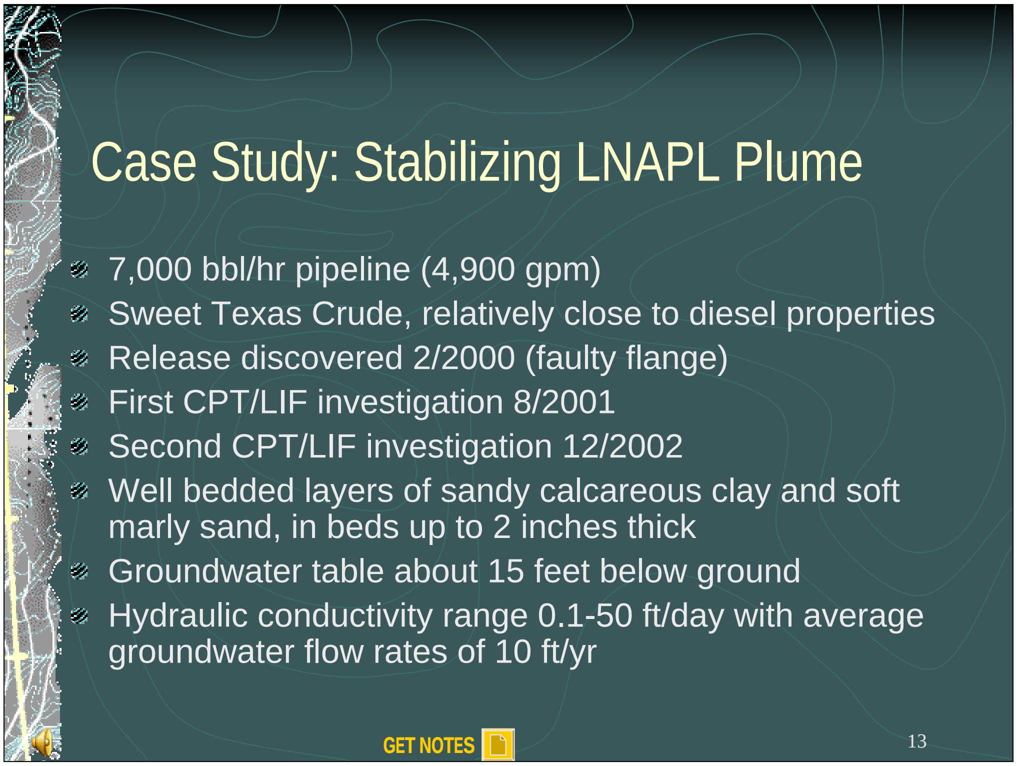
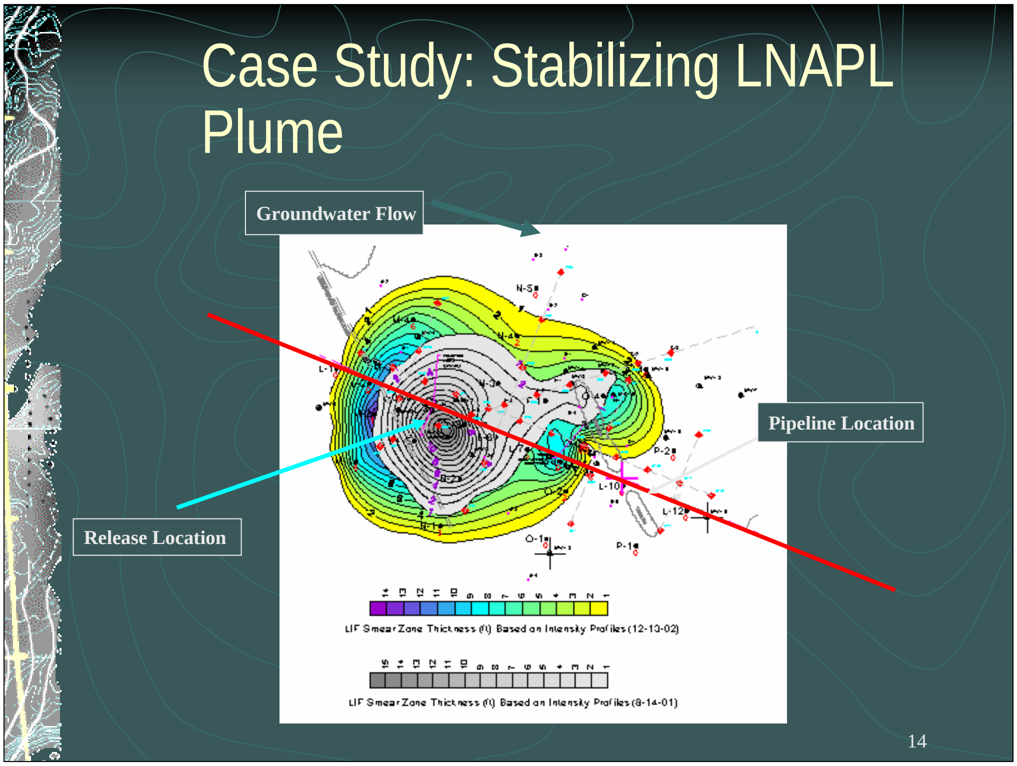


Case study #5 is from a pipeline release from a faulty flange. Pertinent site attributes are shown on this slide.

Comprehensive investigations using borehole geophysics (CPT and LIF, or ROST and LIF) followed by continuous coring and petrophysical work produced a more refined understanding of site conditions.

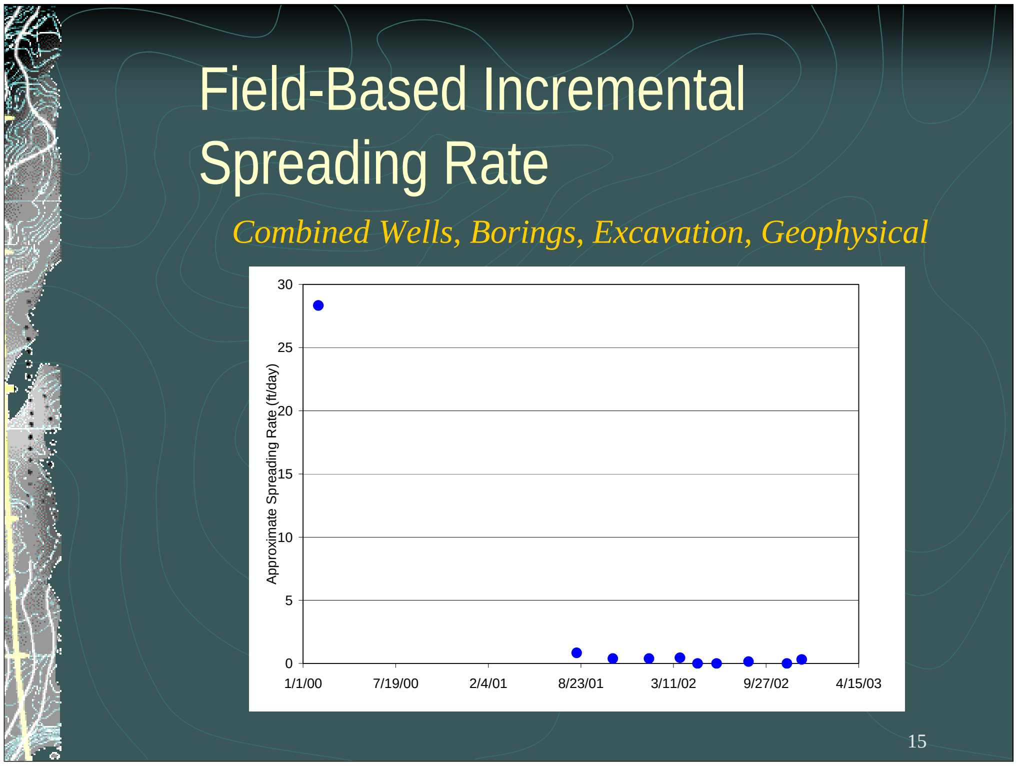
The case study reveals some interesting aspects of LNAPL plume genesis and mobility.



The change in the LNAPL plume footprint (i.e., smear zone) is shown at time intervals 1½ years apart (gray versus bluish yellow areas). Key findings are that LNAPL migration did not follow the groundwater gradient, but rather had a radial LNAPL gradient caused by the release.

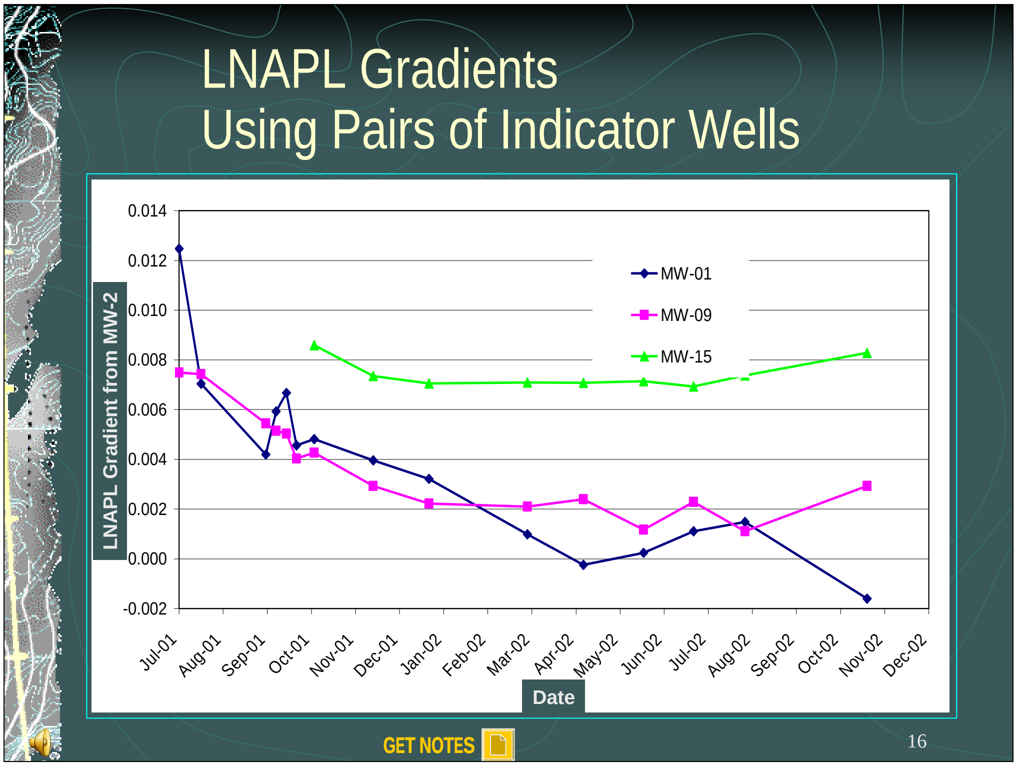
Additionally, a portion of the plume apparently migrated upgradient before coming to a (functionally speaking) immobile condition. (Note that "functionally immobile" refers to a state or condition of the plume where some vertical and lateral redistribution of the LNAPL is acknowledged, but that additional movement is relatively minor and should not impact ongoing plume management objectives).

Unimpacted wells located around the periphery of the LNAPL footprint are monitored on a routine basis. To date, they have not shown that LNAPL expansion has occurred. Dissolved phase compounds are monitored routinely as well. They also indicate that LNAPL is reaching a stabilized footprint around the smear zone.



The initial rate of LNAPL movement appeared to exceed groundwater flow by 1 to 2 orders of magnitude during the initial spreading period, which was up to 25 feet/day for the LNAPL versus approximately 10 feet/year for groundwater. Spreading quickly ceased, however, as the driving forces (LNAPL gradient) dissipated and combined with other factors that resulted in the functionally immobile condition that is observed today.

Data points were determined using all available information indicating the presence of LNAPL, including soil samples, geophysical results, and well gauging/analytical history. The uncertainty in the early time range (~ 2/1/00) of estimated movement simply reflects that the date of release is known within a few weeks, but not precisely. But we do know some pipeline specifics (i.e. volume of transport etc.), and we know what the interim soil excavation sampling showed, in terms of plume distribution, following the release.



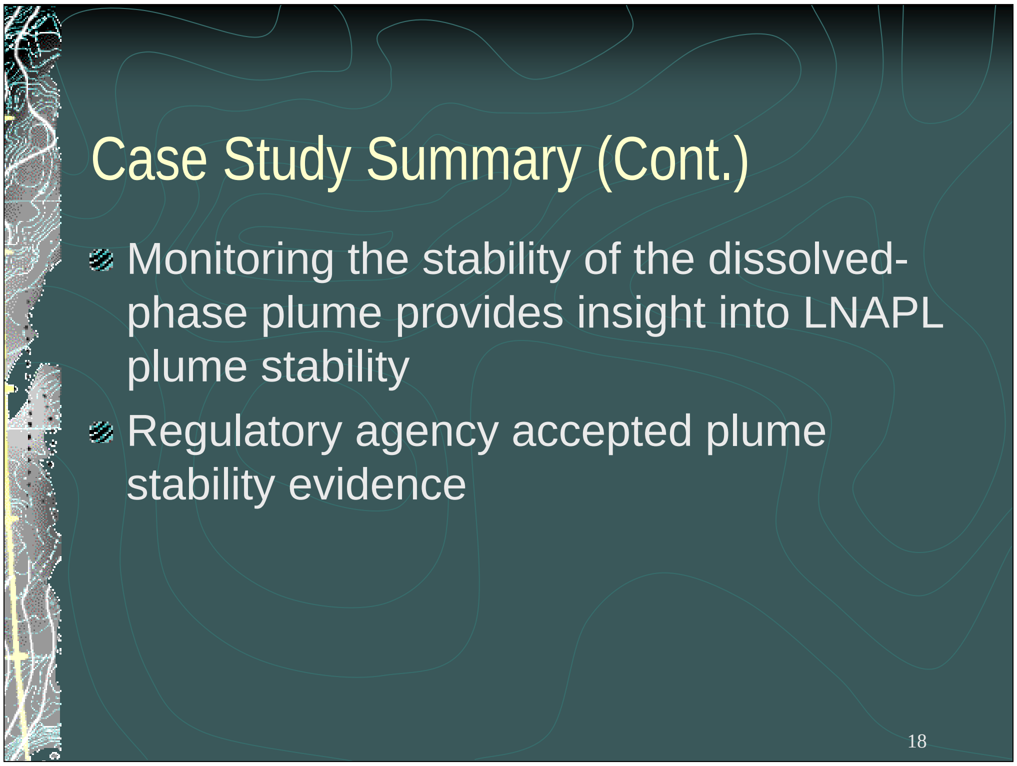
This figure shows how LNAPL gradients between selected monitoring wells (MWs) generally are declining over time. MW-2 (on the vertical axis) is located near the release area. Data from MW-2 is paired with other wells (MWs 1, 9, and 15) that are located within the LNAPL smear or source zone to show how LNAPL gradients have declined over time.

LNAPL gradients were measured between these wells approximately 1 1/2 years after the release (about July 2001) and indicate that at least one order of magnitude decline (0.01 ft/ft to 0.001 ft/ft) generally occurred in less than one year (July 2001 to May 2002). In fact, the rate of gradient decline appeared to be more rapid, leading up to the initial values measured and plotted on this figure (i.e. July 2001). In this field example, MWs 1, 9, and 15 get progressively farther from MW-2. The flat or increasing gradient (as the distance between the release point near MW-2 and the other monitoring wells increases) indicates that there may be localized mounding of LNAPL as the index distance increases. Note that the rather flat-trending LNAPL gradient that exists between MW-2 and MW-15 (which are over 500 feet apart) shows that some of this expected variation will exist between points over time. These slight variations in a nearly steady profile should not be sufficient to cause further migration of the plume downgradient, as illustrated by the spreading-rate data reported in the previous slide and by more recently collected data.

Because LNAPL gradients are required to provide a driving force for the LNAPL, it appears that a decline in this parameter is one of the primary reasons this plume has reached an immobile condition.

Case Study Summary

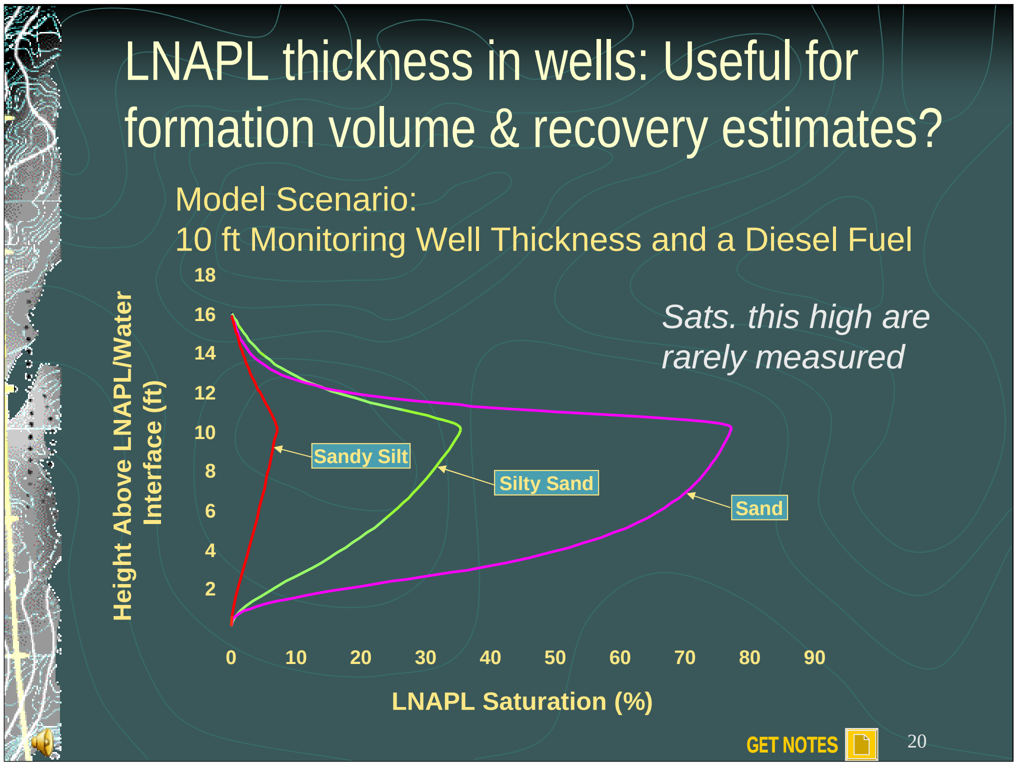
- LNAPL flow did not follow the groundwater gradient, but rather a radial pattern caused by the release.
- The initial rate of LNAPL movement exceeded groundwater flow rates by 1-2 orders of magnitude during the initial spreading period.
- Although the plume spread rapidly during initial stages, it ceased significant movement relatively quickly after that period (within 2-3 years).
- Similarly, LNAPL gradients were shown to dissipate quickly after the release period.



Highlight that a demonstration of plume stability does not equal no further action. Demonstration of LNAPL plume stability is a step on the overall LNAPL framework

LNAPL Migration Summary

- Detailed field & modeling studies show that after a release is stopped, LNAPL plumes soon become immobile because:
  - the LNAPL gradient dissipates
  - the effective conductivity diminishes
  - pressure within pores at the leading edge of the plume eventually resist LNAPL entry
- Some LNAPL plumes have not reached equilibrium.
  - recent or ongoing releases
  - karst geology
  - highly stratified sites
- Numerous cases of stable dissolved plumes suggests that many LNAPL plumes are practically immobile.

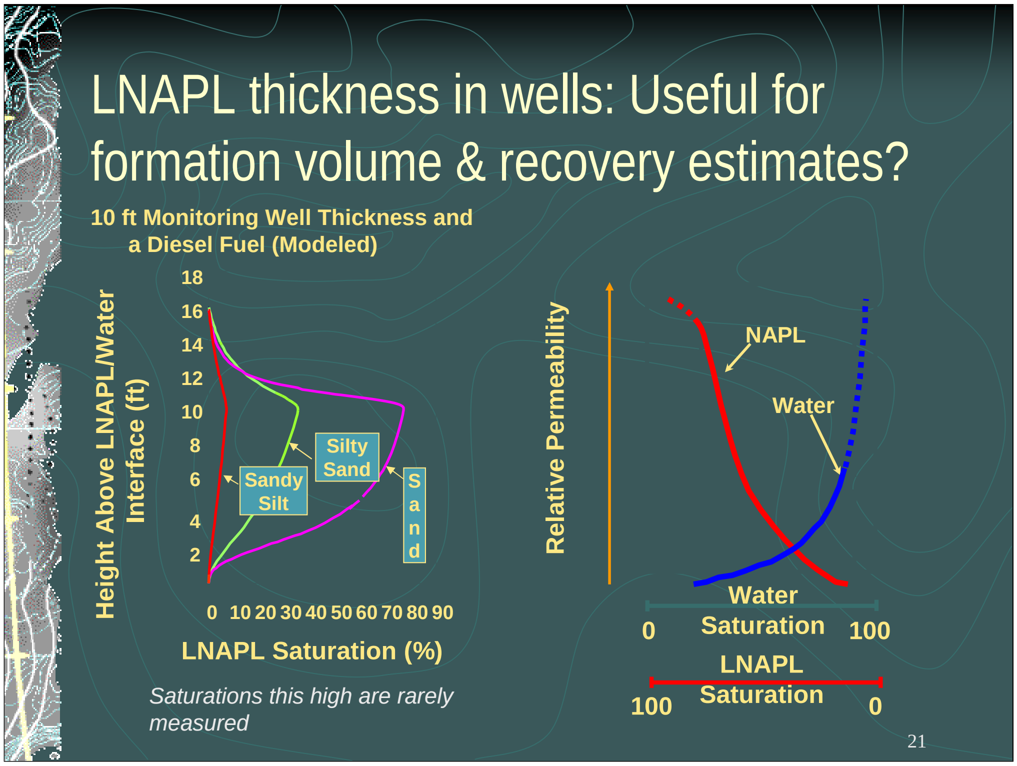


Grain size determines the LNAPL saturation distribution. For a given grain size, LNAPL thickness in a monitoring well, and LNAPL-water combination, we can calculate the LNAPL saturation for different grain sizes using the capillary pressure parameters.

This figure was generated using a LNAPL thickness of 10 feet in the monitoring well and diesel LNAPL-water combination. In the figure, we can see that, in sandy silt, the maximum LNAPL saturation with a LNAPL thickness of 10 feet is only about 7%. In a sand with the same LNAPL thickness in the monitoring well, LNAPL saturations can reach 77%. We understand from our previous discussions of capillary pressure that, in the sand, LNAPL can displace water much more easily than in the silt. Thus, higher LNAPL saturations are possible.

In practice, high LNAPL saturations are rarely measured. Of 212 analyses performed at BP refining sites, the highest saturation found was 56%. 83% of all samples had LNAPL saturations lower than 10%. In fine-grained media, maximum saturations were typically 2-5%; in coarse-grained media, maximum saturations typically were 10-56%.

API has compiled a ***Light Non-Aqueous Phase Liquid (LNAPL) Parameters Database***. In general, LNAPL capillary pressure parameters appear to be different than for agricultural soils whose capillary pressure curves are often used to calculate saturation distributions. It is speculated that the difference is caused by the compaction of porous media at LNAPL sites. This difference probably also leads to the difference between the maximum saturations calculated with default parameters.



The figure on the left shows that different soil types with different LNAPL saturations can produce the same LNAPL thickness in a well. Is there a large volume of LNAPL in the formation because there is 10 feet of LNAPL standing in a well? It depends on the soil type. Grain size determines the LNAPL saturation distribution. For a given grain size, LNAPL thickness in a monitoring well, and LNAPL-water combination, we can calculate the LNAPL saturation for different grain sizes using the capillary pressure parameters.

The figure on the left was generated using a LNAPL thickness of 10 feet in the monitoring well and diesel LNAPL-water combination. In the figure, we can see that, in sandy silt, the maximum LNAPL saturation with a LNAPL thickness of 10 feet is only about 7%. In a sand with the same LNAPL thickness in the monitoring well, LNAPL saturations can reach 77%. We understand from our previous discussions of capillary pressure that, in the sand, LNAPL can displace water much more easily than in the silt. Thus, higher LNAPL saturations are possible.

Integratin

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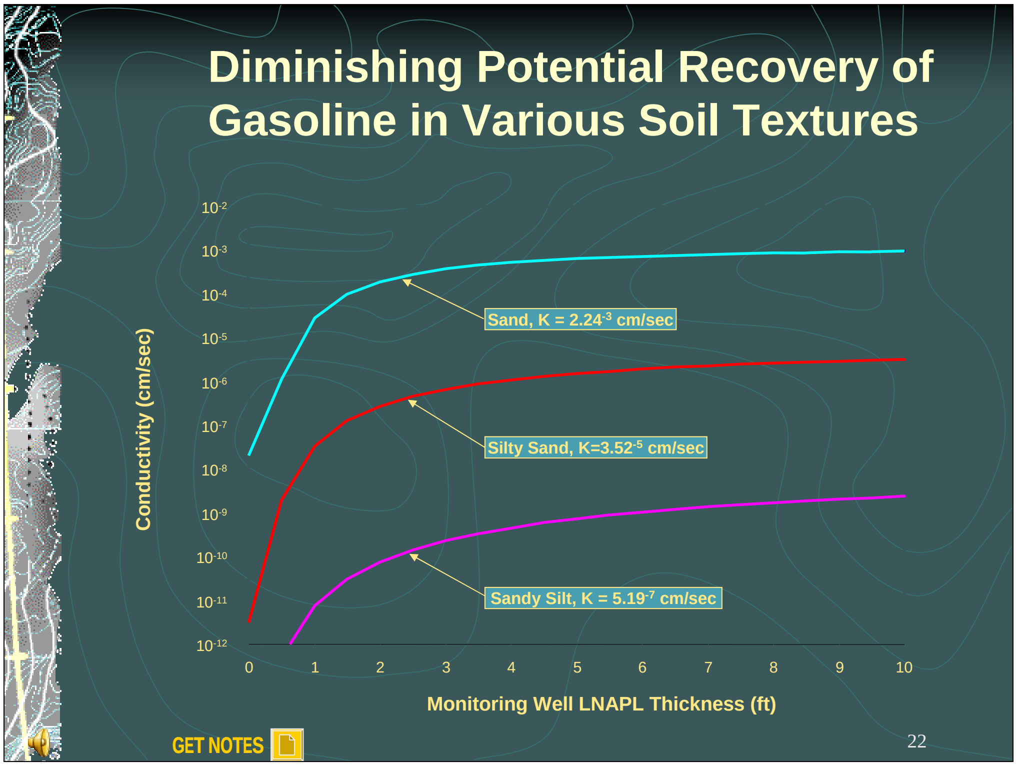
Assuming the saturations from the figure on the left, what does the well LNAPL thickness tell us about potential recovery? In the case of the sandy silt, the relative permeability is very low at 7% LNAPL saturation. Initial LNAPL recovery may be better for the sandy soil at higher saturations due to higher relative permeability.

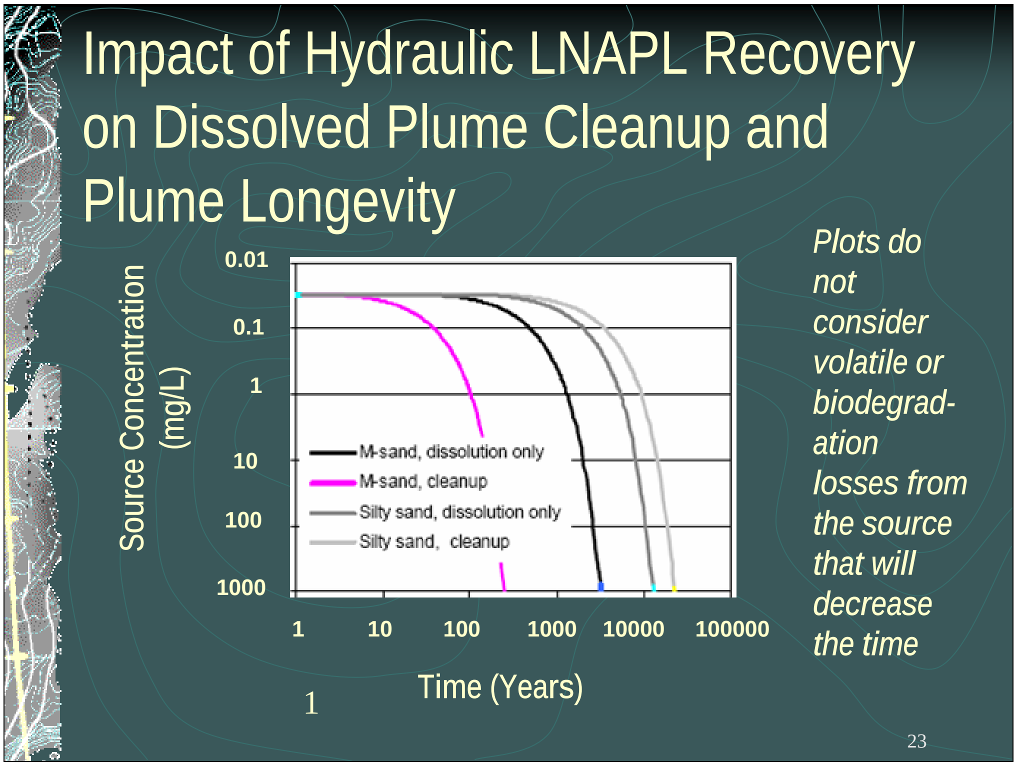


Recovery gets tougher below the inflection point.

We're trying to identify the point of diminishing returns; it applies to all remediation activities

This slide shows the vertically averaged value of LNAPL conductivity, which varies along the LNAPL saturation curve, at different monitoring well thicknesses in three porous media. The Burdine model and gasoline fluid properties were used in these calculations.

LNAPL conductivity is largely a function of the permeability of the porous media. It is clear, however, that the conductivity of LNAPL decreases by orders of magnitude as the thickness of LNAPL in a monitoring well and its volume in the subsurface decrease. This is why recovery of LNAPL is so difficult when well thickness is small.



The plots illustrate the relative benefit of hydraulic recovery vs. no recovery for 2 soil types. Source concentration refers to the dissolved concentration at the immediate downgradient edge of the source. Hydraulic recovery continues until saturations reach residual.

In the case of the medium sand, the time to reduce concentrations by over 4 orders of magnitude will be cut by an order of magnitude. The time difference in the silty sand case between remediation and no remediation may not be significant in many cases.

Summary

- The revised model of LNAPL distribution in porous media provides a better explanation for observations of:
  - LNAPL plume migration and stabilization
  - Recovery volume and rates
- Not all LNAPL is hydraulically recoverable; some residual will remain
  - Coping with residual LNAPL is an important component of any LNAPL remediation or management strategy
- The improved LNAPL conceptual model provides a basis for improved decision making.
  - Application on RTDF Framework
  - LNAPL site conceptual model (LSCM) development

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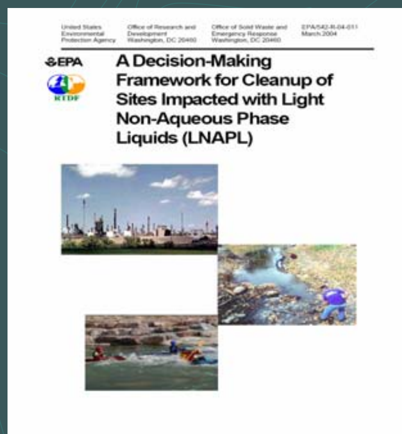
The RTDF Decision Framework


United States Environmental Protection Agency | Office of Research and Development Washington, DC 20460 | Office of Solid Waste and Emergency Response Washington, DC 20460 | EPA/542-R-04-011 March 2004

EPA

RTDF

A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL)

- Developed by stakeholders who share an interest in pursuing technical and decision - making solutions for addressing large-scale LNAPL contamination.
- Download at: http://www.rtdf.org/public/napl/publications/

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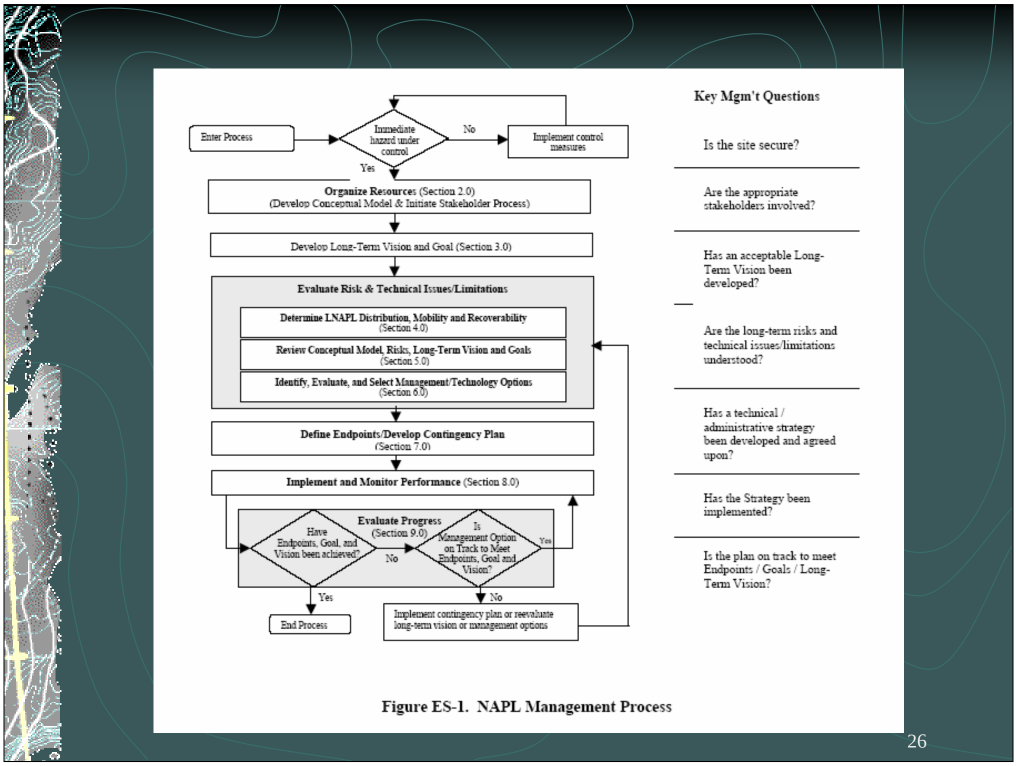
Key Mgm't Questions
Immediate hazard under control
Enter Process
No
Implement control measures
Yes
Organize Resources (Section 2.0)
(Develop Conceptual Model & Initiate Stakeholder Process)
Develop Long-Term Vision and Goal (Section 3.0)
Evaluate Risk & Technical Issues/Limitations
Determine LNAPL Distribution, Mobility and Recoverability (Section 4.0)
Review Conceptual Model, Risks, Long-Term Vision and Goals (Section 5.0)
Identify, Evaluate, and Select Management/Technology Options (Section 6.0)
Define Endpoints/Develop Contingency Plan (Section 7.0)
Implement and Monitor Performance (Section 8.0)
Evaluate Progress (Section 9.0)
Have Endpoints, Goal, and Vision been achieved?
No
Is Management Option on Track to Meet Endpoints, Goal and Vision?
Yes
Yes
No
End Process
Implement contingency plan or reevaluate long-term vision or management options
Is the site secure?
Are the appropriate stakeholders involved?
Has an acceptable Long-Term Vision been developed?
Are the long-term risks and technical issues/limitations understood?
Has a technical / administrative strategy been developed and agreed upon?
Has the Strategy been implemented?
Is the plan on track to meet Endpoints / Goals / Long-Term Vision?
Figure ES-1. NAPL Management Process
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Definitions

Long-Term Vision	A qualitative statement of the ultimate desired situation/condition at the site once specific actions are taken and specific goals are accomplished.
Goal	Describe what is needed to obtain the long-term vision. Goals should be reasonable, practical, and as specific as possible.
Endpoints	Provide metrics to measure achievement of specific LNAPL management /remediation goals.

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Examples

	Scenario 1	Scenario 2
Long-Term Vision	Return to residential reuse	Community golf course
Goal	Excavation of all LNAPL contaminated soils	No further LNAPL or dissolved plume migration
Endpoints	- Soil samples < state residential standards - GW returned to acceptable use	Sentinel wells confirms plume stability

The Importance of Establishing a Long-Term Vision

- Gets stakeholders on the same page
- Begin to flesh-out what is achievable
- Sets the stage for discussing goals and endpoints
- Long-term vision may be revised if goals are later found not achievable
- A long-term vision can be developed for operating or inactive sites

What Types of Goals May be Important?

- Compliance with existing regulations and rules
- Achieving beneficial land use
  - Intermediate
  - Long-term
- Reducing risk by managing exposures
- Returning aquifers to maximum beneficial use
- Non-Risk Drivers
  - Aesthetic issues

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Sites May Have Several Goals for Different Time Frames

Intermediate-Term	Verify LNAPL footprint stability or reduced mobility by the year 2007 [add another example]
Long-Term	Achieve risk-based standards at the property boundary by the year 2009 [add another example]

Goals Are Not Set In Stone

- Further evaluation of endpoints may indicate that they are not achievable and require parties to adjust the goals.

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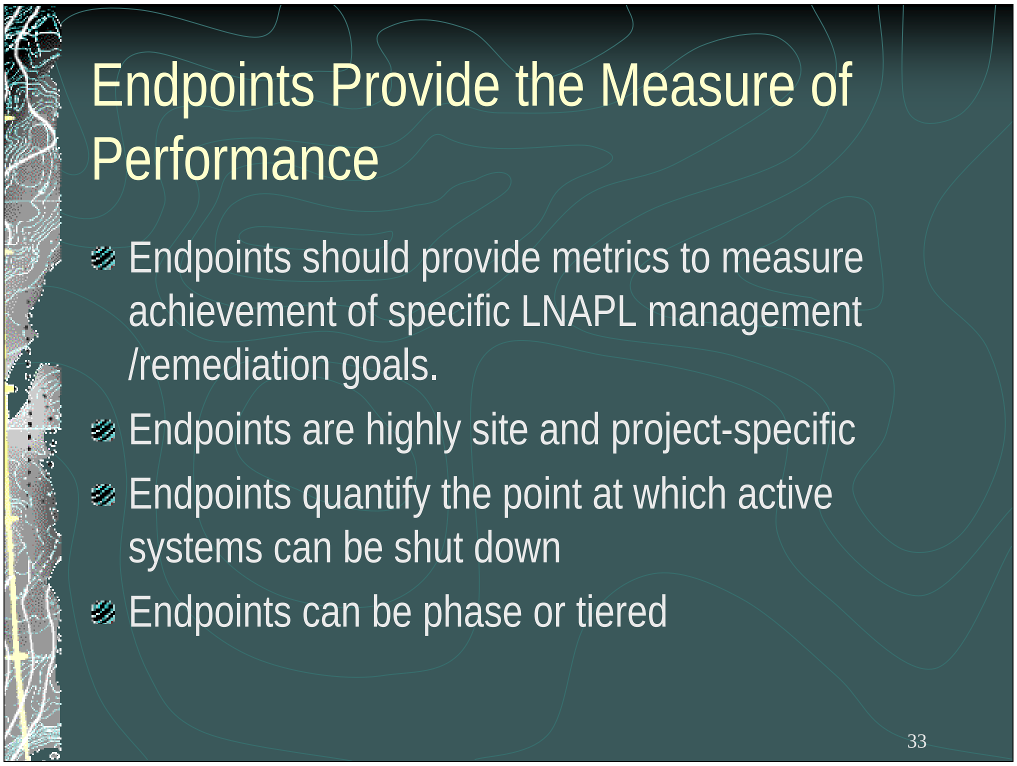

Endpoints are highly site and project-specific, but some states may require MCLs to be met in certain places at all of their sites.

One or More Endpoints May Be Necessary for Each Goal

Remediation Goal	Example Endpoints
Protect downgradient drinking water supply	Achieve MCLs 100 ft. before property line
Reduce LNAPL mobility to de minimus levels	- LNAPL velocity potential < 1 x 10-6 cm/s - No discernable LNAPL footprint movement - LNAPL transmissivitiy < 1x10-5 ft2/day
Reduce the longevity of COCs in the LNAPL	- Reduce benzene longevity to less than 30 years at a specific concentration at a specific point of compliance - Accelerate the rate of mass loss to 5 x than natural processes alone

Endpoints Should Be Defined With Specific Considerations Including:

- Type of measurement
- Method for sample collection
- Analytical method
- Location of measurement
- Timeframe for measurements
- Number of measurements and data analysis/presentation (e.g., statistics)

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Decision / Assessment Guides That Supplement the RTDF Framework

ASTM "Standard Guide for Conceptual Model Development and Remediation Decision-Making for LNAPL Released to the Subsurface"	LNAPL site conceptual development Metrics for remediation goals and option selection
API Interactive LNAPL Guide	Primers Assessment tools for mobility, recoverability, metrics

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Wrap-up

- Improved scientific and technical understanding has led to an improved LNAPL conceptual model which recognizes:
  - challenges of complete LNAPL removal
  - implications of remaining residual mass
  - current or eventual stability of most plumes
- The RTDF NAPL Alliance has created a framework to address LNAPL site management which:
  - Is flexible enough to integrate with state programs and risk / non-risk drivers
  - Focuses on stakeholder-developed long-term vision first
  - Leads to technically practicable LNAPL management goals that can be quantified with measurable endpoints
- Peer-reviewed and field-tested tools and guides are currently available
- A variety of training packages are available or under development

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Alternative slides
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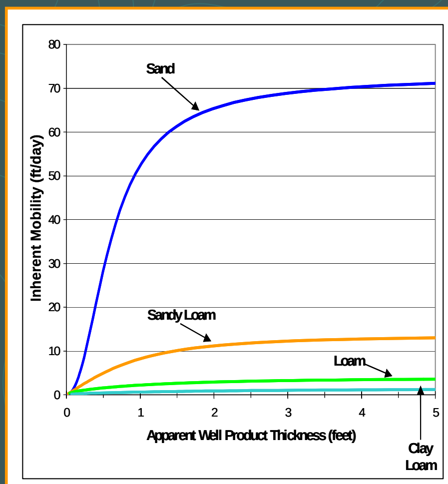
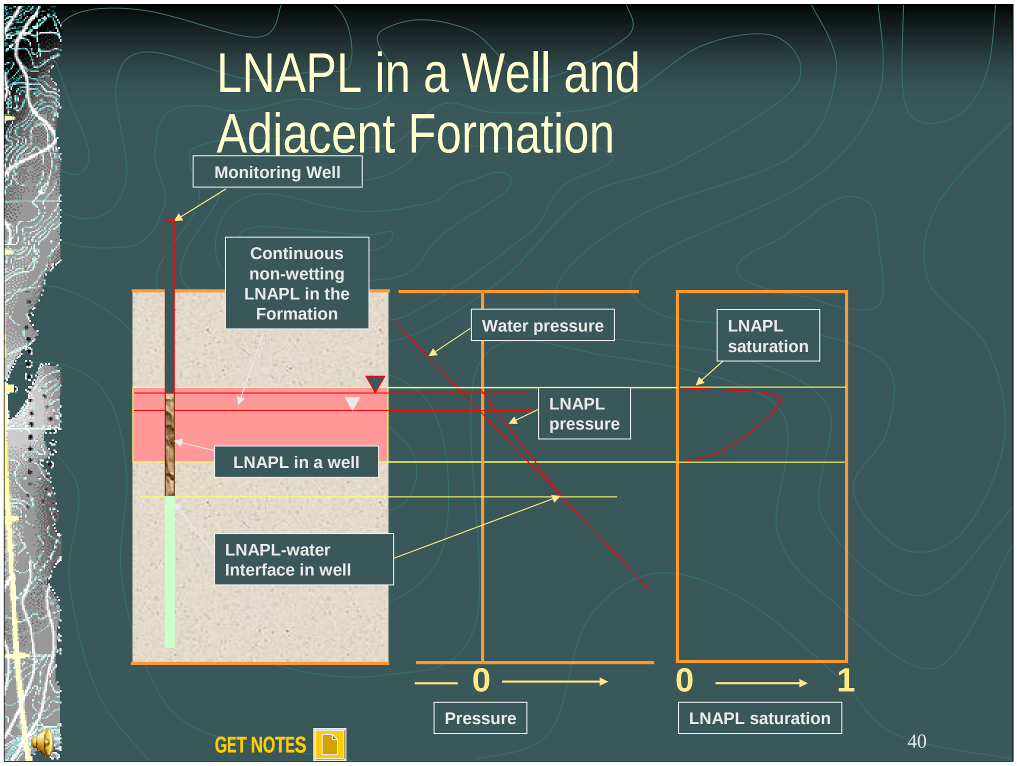
Diminishing Recovery of Gasoline in Various Soil Textures



- Recovery gets tougher below the inflection point
- We're trying to identify the point of diminishing returns; it applies to all remediation activities

39



Alternative to previous slide

Before we discuss the calculation of LNAPL saturation distribution in the subsurface, it would be useful to examine the complex relationship between LNAPL thickness in a well and the volume of LNAPL in the formation. This figure from **API** follows Farr et al (1990). It presents a simple case in which LNAPL has migrated laterally into a uniform porous media where the water table is stable. The left-hand panel shows that LNAPL in a well extends below the LNAPL in the formation. Within this extension, the pressure difference between the LNAPL in the well and the water in the formation is not great enough to push the water out of the formation. In other words, the capillary pressure is less than the displacement pressure. The extension of LNAPL in the well below the elevation in the formation increases as the porous media become finer and as the densities of the liquids become more similar.

The center panel of this figure focuses on the pressures in the surficial aquifer in relation to the LNAPL thickness measured in the monitoring well. If LNAPL is present in the aquifer, the LNAPL surface (or LNAPL table) occurs at the air-LNAPL interface. The thickness of LNAPL in the well is the difference between the air-LNAPL interface elevation and the water-LNAPL interface elevation. LNAPL pressure starts at atmospheric pressure at the air-LNAPL interface and increases with depth. However, because the LNAPL has a different density than water, the LNAPL pressure gradient is different than the water pressure gradient. The LNAPL and water gradients intersect where the LNAPL and water pressures are equal, which establishes the water-LNAPL interface. The pressure difference between LNAPL and water at any given depth is the LNAPL-water capillary pressure.

The right-hand panel of the figure illustrates that the fraction of the pore space filled (saturated) with LNAPL changes vertically. Moving upward from the LNAPL-water interface, the pressure difference between the LNAPL and the water increases. As this occurs, the LNAPL saturation increases. When air begins to occupy pore space along with LNAPL and water, which occurs at the top of this figure, LNAPL saturation decreases.