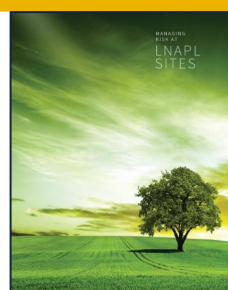
LNAPL BEHAVIOR AND EVALUATION IN THE SUBSURFACE

(WITH AN EMPHASIS ON NATURAL SOURCE ZONE DEPLETION)

REMTECH 2019
Banff, Canada
October 17, 2019

GSI ENVIRONMENTAL



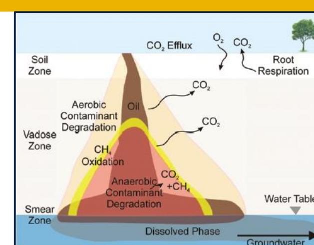
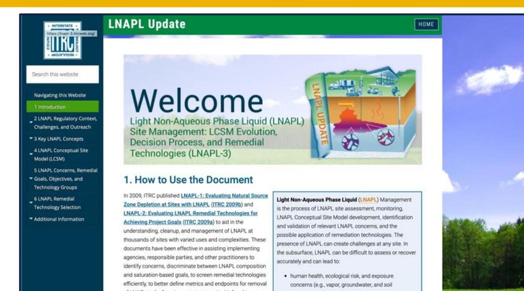


Fig. 1. Conceptual model of contamination in the vadose zone at the Bemidji site.



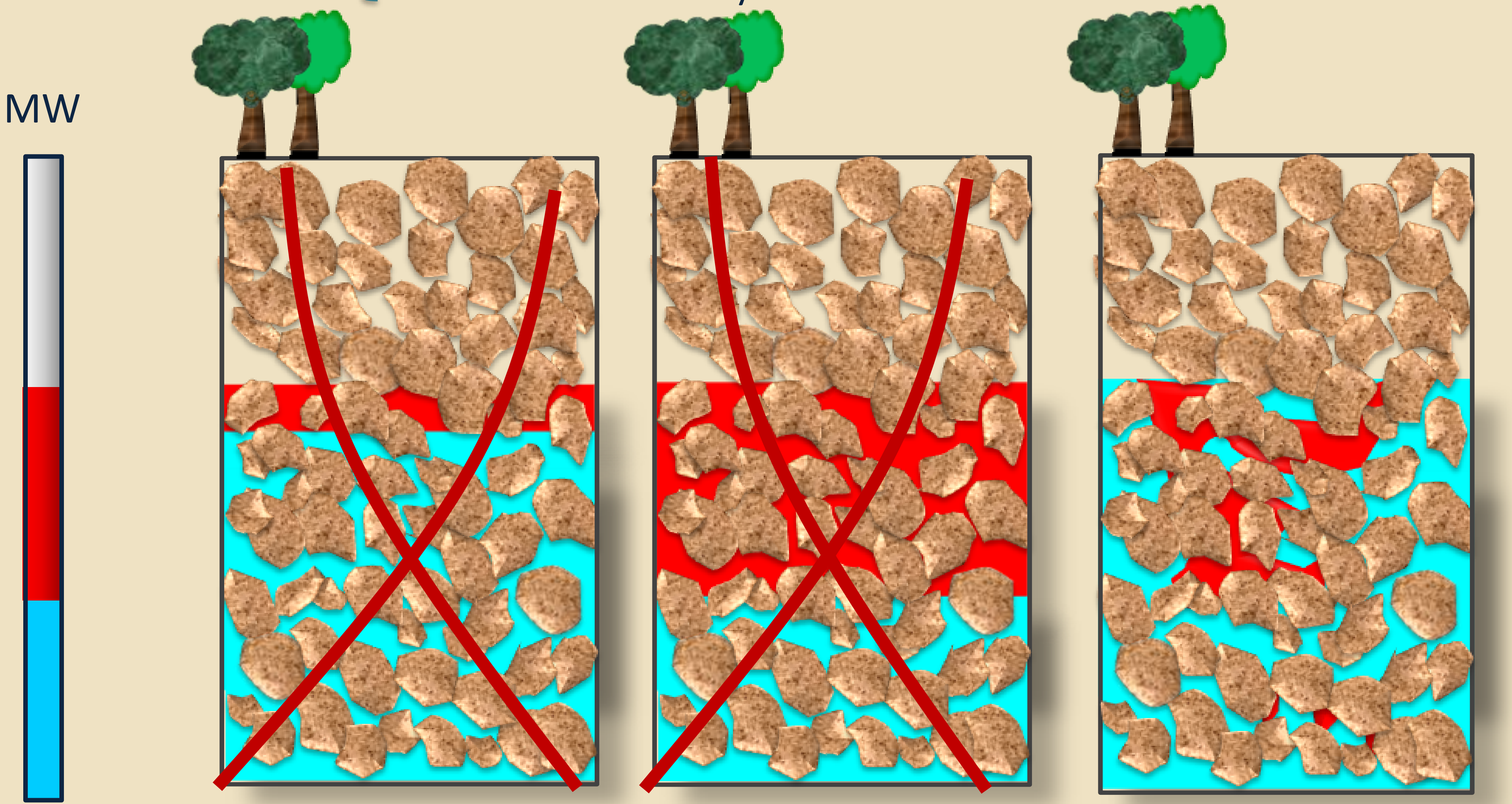
Curtis C. Stanley and Charles J. Newell,
GSI Environmental, Houston, Texas, USA

"THE TIMES THEY ARE A CHANGIN"

JUST ASK BOB DYLAN

Outdated Concepts

- Pancake Distribution
- LNAPL Lasts Forever
- LNAPL Thickness Key Metric



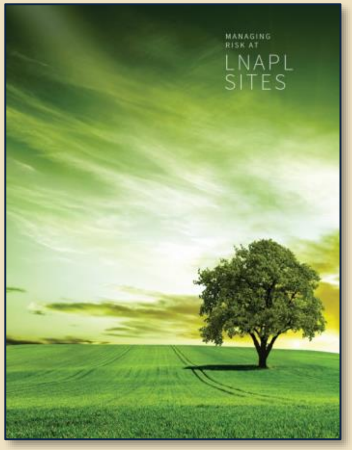
ACTUAL LNAPL CONCEPTUAL MODEL

1. **LNAPL apparent thickness in wells ≠ risk**

2. **LNAPL attenuates much more quickly than once thought due to Natural Source Zone Depletion (NSZD)**

3. **LNAPL plumes reach a state of residual saturation once the release stops more quickly due in part to NSZD**

4. **NSZD means most or almost all LNAPL bodies from historic releases (more than a decade old) are likely stable or shrinking at this time. LNAPL bodies tend to quickly reach a state of residual saturation once the release has stopped.**



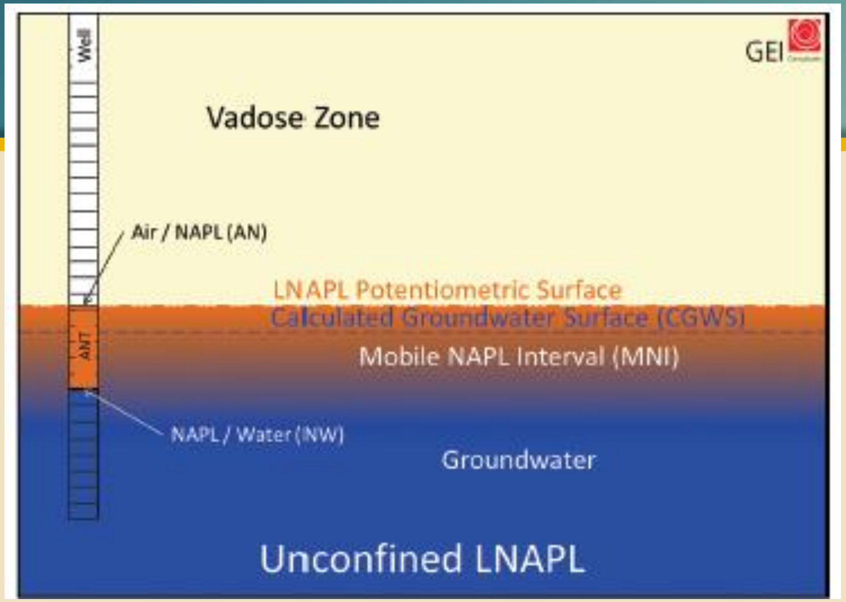

Groundwater Monitoring&Remediation

Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change

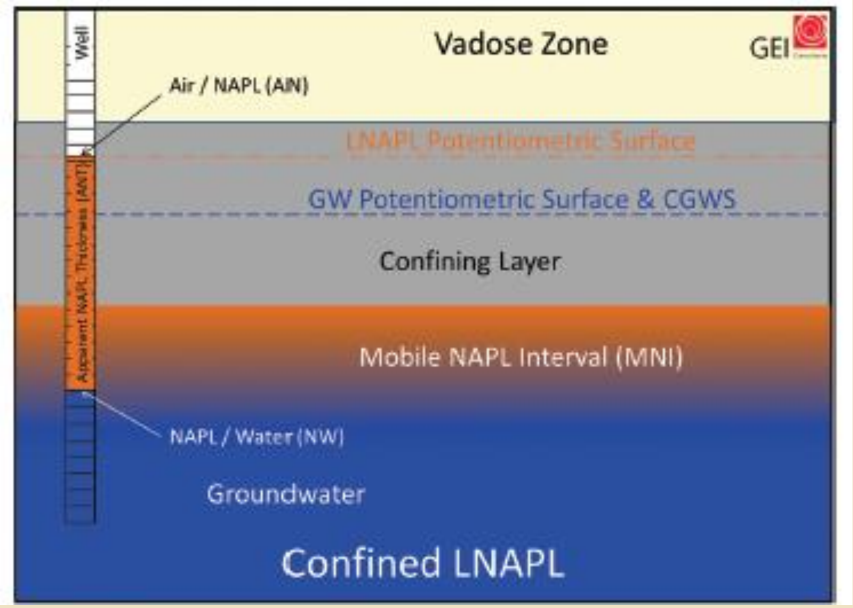
by Sanjay Garg, Charles J. Newell, Poonam R. Kulkarni, David C. King, David T. Adamson, Maria Irianni Renno, and Tom Sale

1. LNAPL Apparent Thickness in Wells ≠ Risk

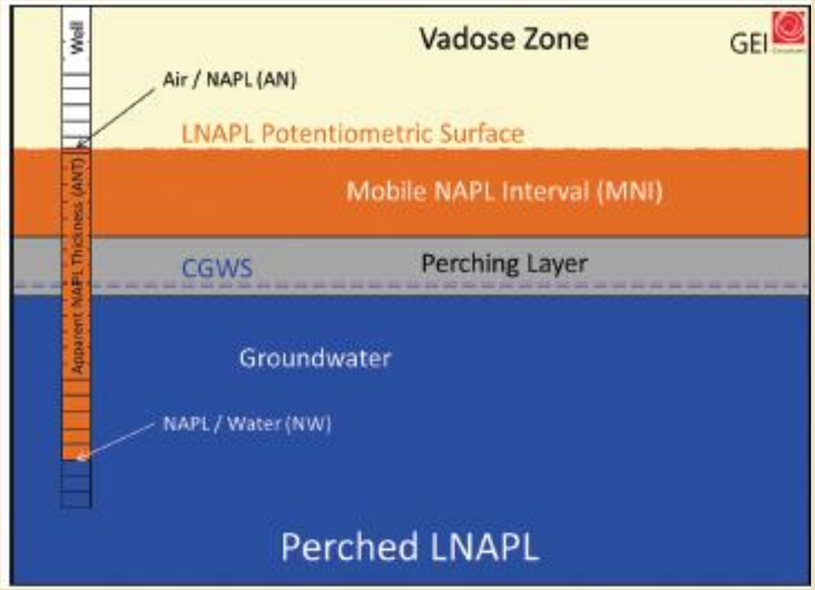
As shown in these three scenarios, the physical setting can create LNAPL thicknesses in wells that are misleading with respect to the amount of LNAPL in the formation or the configuration of the mobile LNAPL interval



Scenario 1: Unconfined LNAPL



Scenario 2: Confined LNAPL



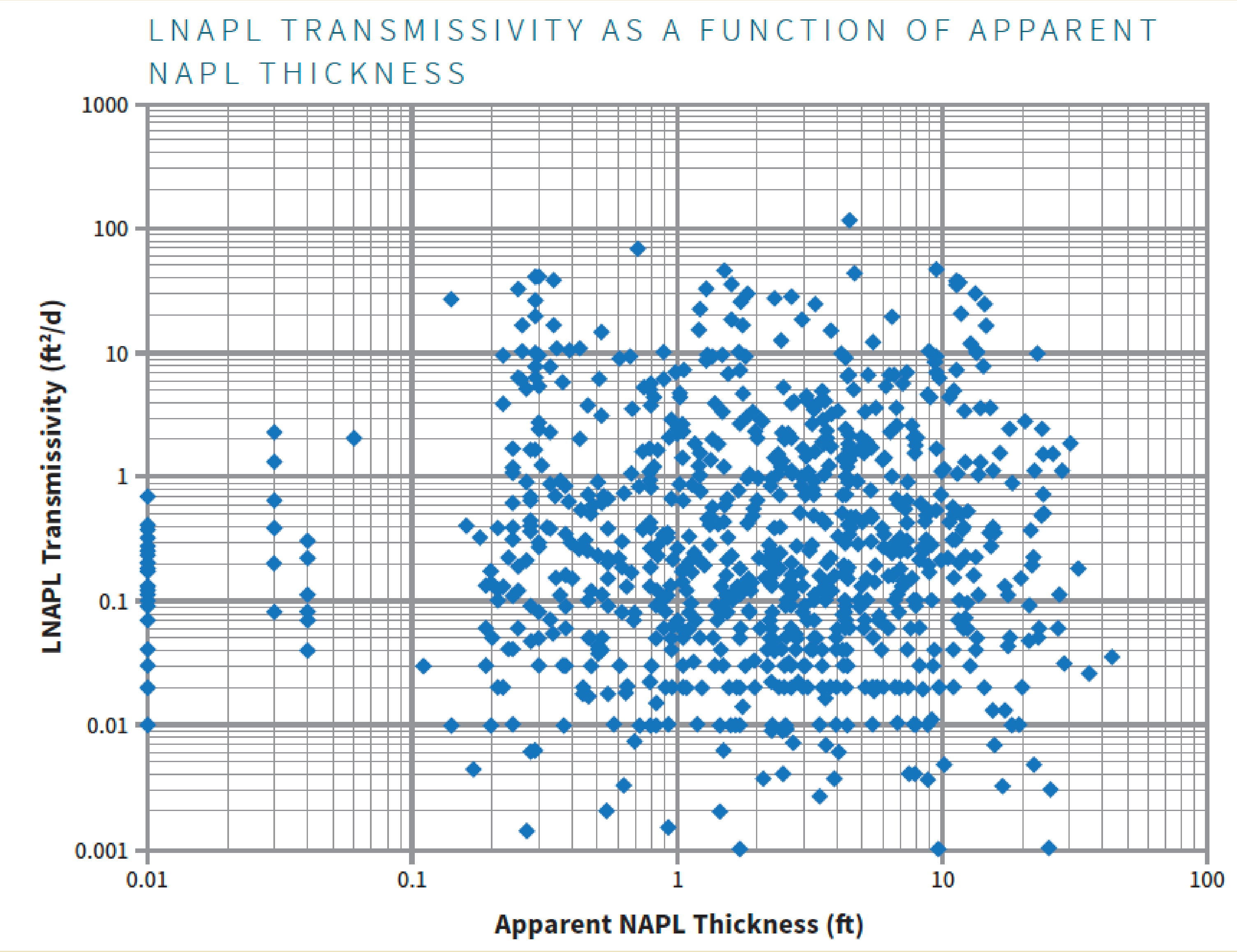
Scenario 3: Perched LNAPL

LNAPL FAQ. Sale, Hopkins, Kirkman, 2018

1. LNAPL Apparent Thickness in Wells ≠ Risk

LNAPL transmissivity is not a function of LNAPL thickness in a well.

It is controlled by the LNAPL saturation, the nature of the geologic material, and groundwater fluctuation.

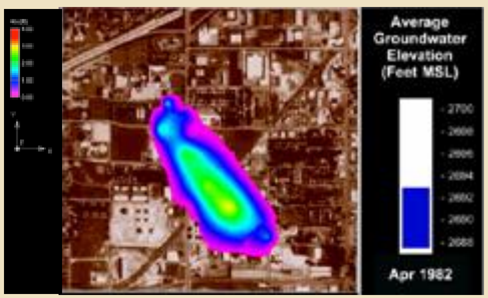


LNAPL FAQ. Sale, Hopkins, Kirkman, 2018

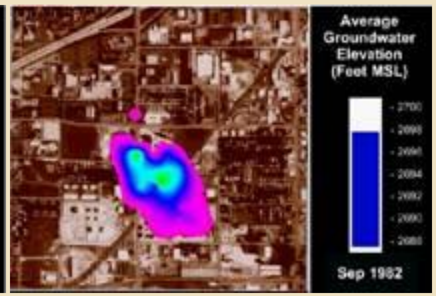
1. LNAPL Apparent Thickness in Wells ≠ Risk
EXAMPLE SEASONAL LNAPL REDISTRIBUTION

LNAPL Monitoring Over Time at a Refinery

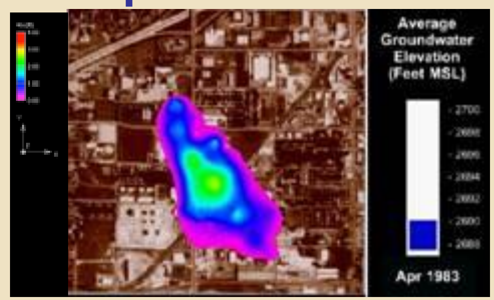
Low Water
April 1982



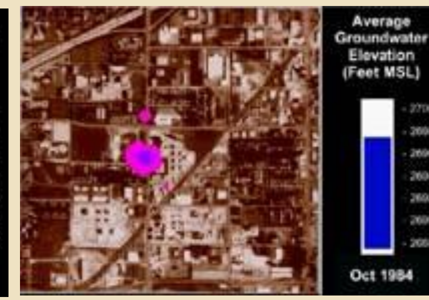
High Water
Sept 1982



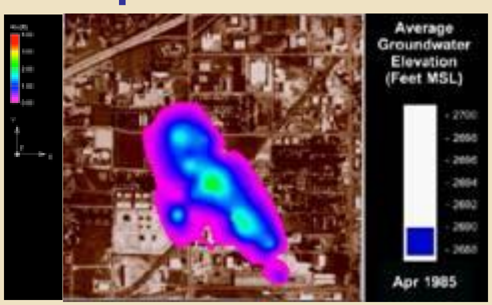
Low Water
April 1983



High Water
Oct 1984

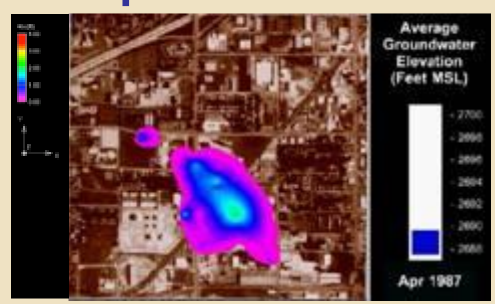


Low Water
April 1985



High Water
Sept 1986

Low Water
April 1987

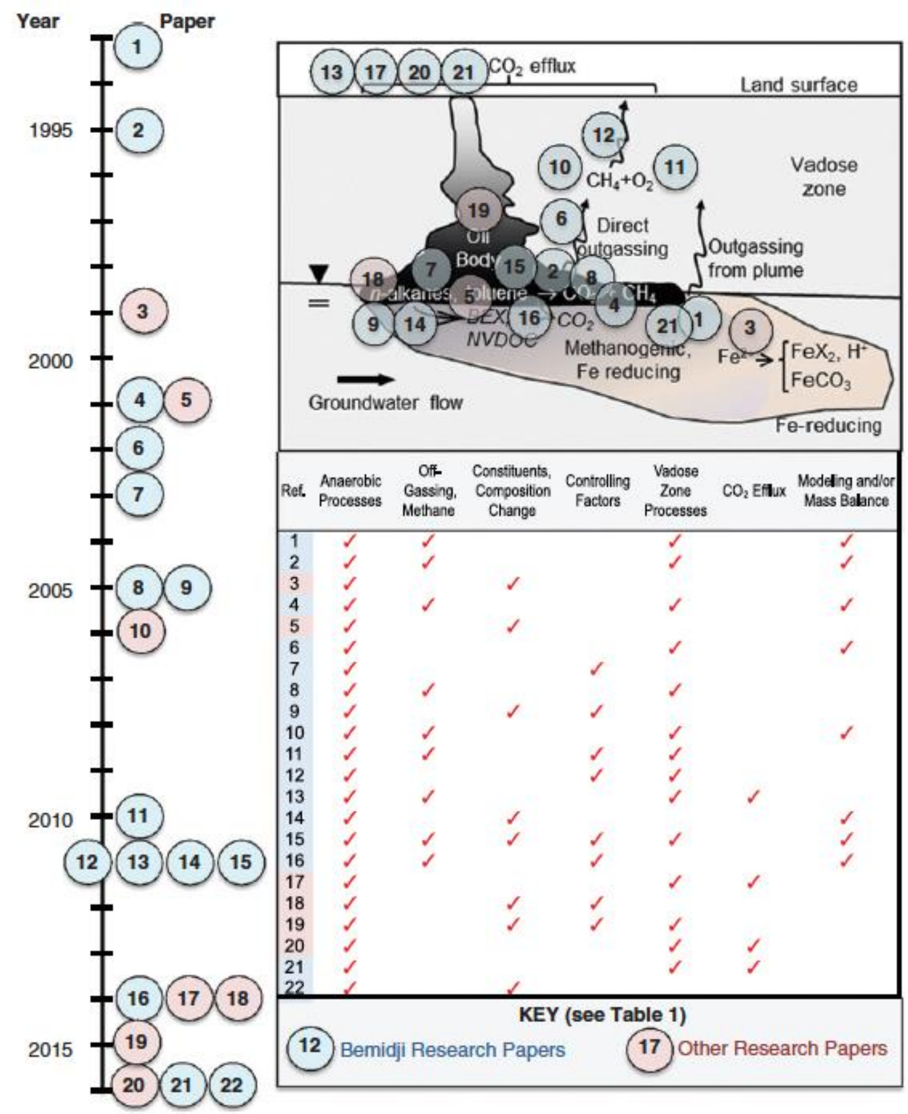


From API Interactive NAPL Guide, 2004

- **Measured LNAPL Depth in Monitoring Wells : 0 to 3 feet**
- **Seasonal Water Table Variation : 8 foot range**

2. LNAPL Attenuates Much More Quickly Than Once Thought Due to Natural Source Zone Depletion (NSZD)

This graphic shows a timeline of 22 key research papers from 1993 to 2016 that revealed that Natural Source Zone Depletion is a key process for managing LNAPL source zones.



Source: Garg et al., 2018

NSZD OVERVIEW
OUTGASSING & EBULLITION

NSZD

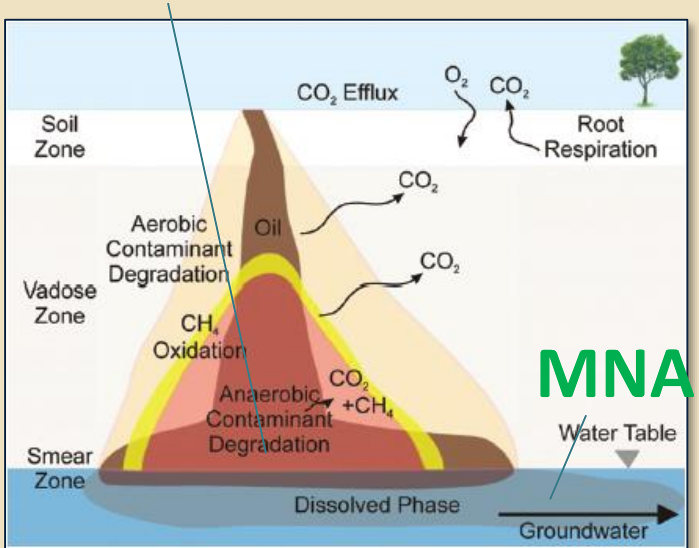


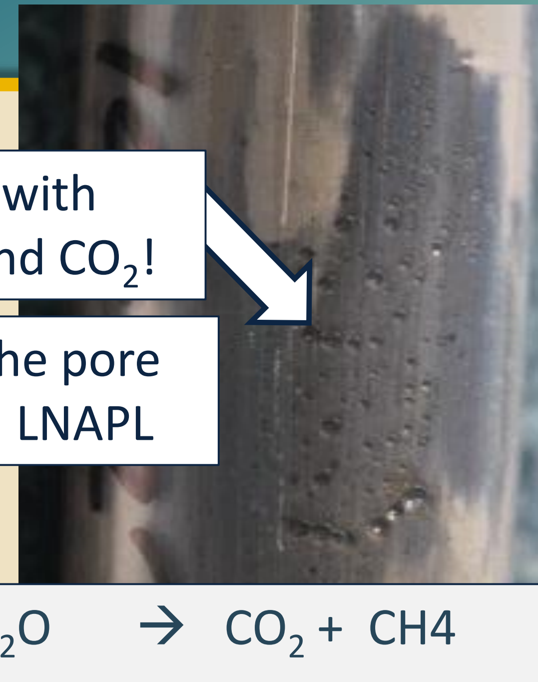
Fig. 1. Conceptual model of contamination in the vadose zone at the Bemidji site.

MNA

Sihota and Mayer, 2011

Bubbles with methane and CO_2!

Occurs in the pore space with LNAPL



Source: *Tom Sale, CSU*

LNAPL+H_2O	→	CO_2 + CH4
CH4 + O2	→	CO_2 + H_2O

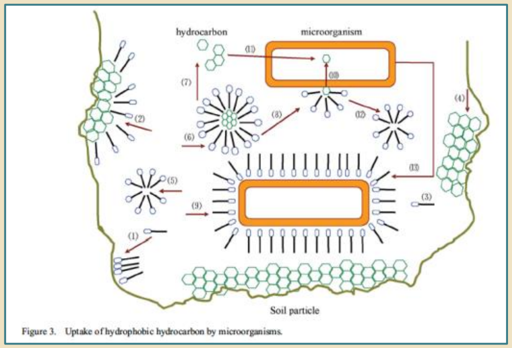
Source: Garg et al., 2018

KEY POINTS

- **MNA focuses on dissolved plume attenuation: how far will plume migrate.**
- **NSZD focuses on source depletion: how long will LNAPL source persist. Methanogenesis is usually the dominant process**

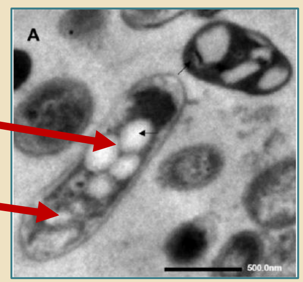
NSZD LNAPL BIODEGRADATION

Three Hydrocarbon Uptake Pathways: 1. From dissolved phase; 2. Contact with submicron oil droplets; 3. Direct contact with large droplets

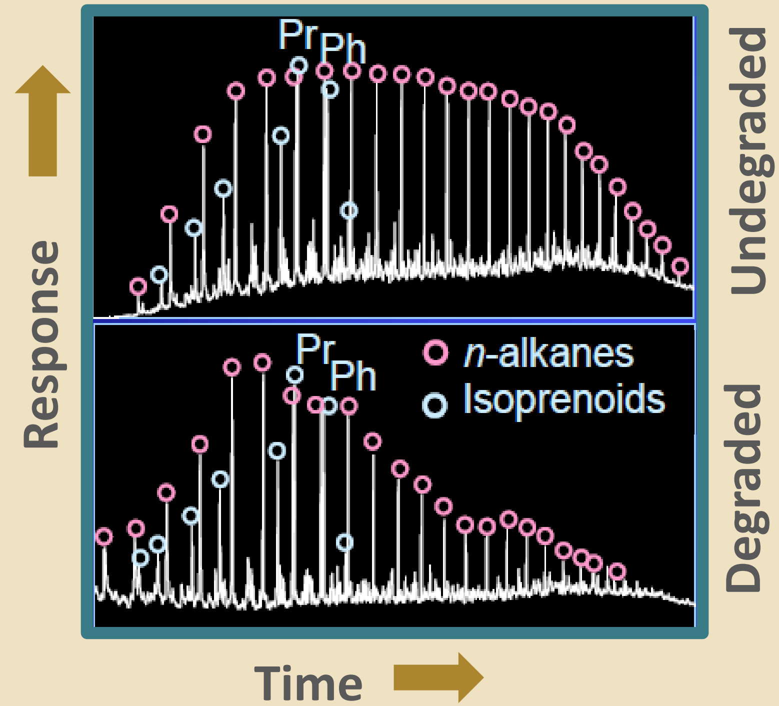


n-octadecane inclusions

Pseudomonas



Hua et al., 2014



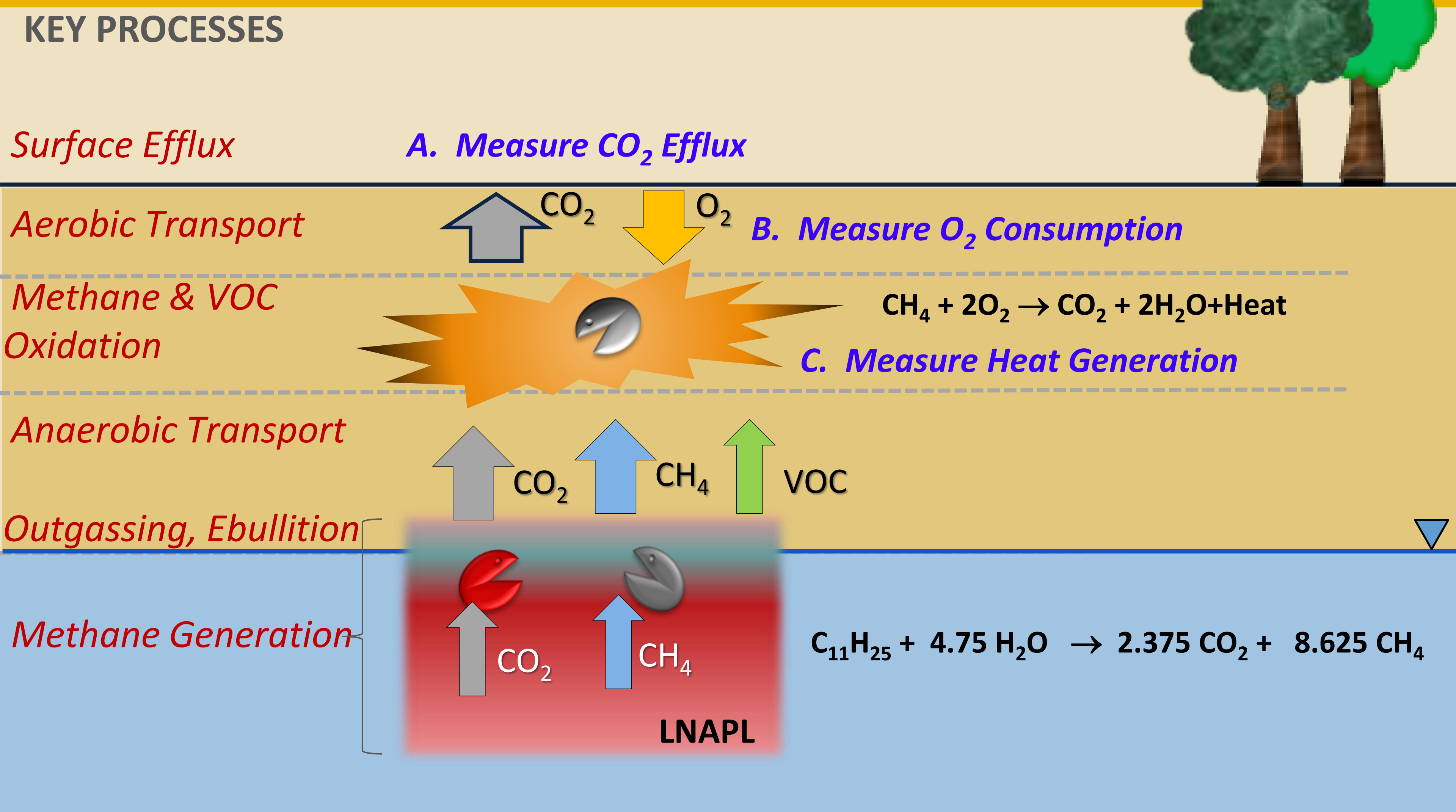
Bekins et al, 2005

KEY POINT

Hydrocarbons don't have to dissolve to biodegrade

Source: Garg et al., 2018

MEASURING NSZD: THREE GENERAL METHODS



Source: Garg et al., 2018

*Note: size of arrows indicates magnitude of flux

MEASURING NSZD: THREE GENERAL METHODS

A. *Measure CO_2 Efflux*

Dynamic Closed Chamber (LI-COR)

Carbon Traps

B. *Measure O_2 Consumption (Gradient Method)*

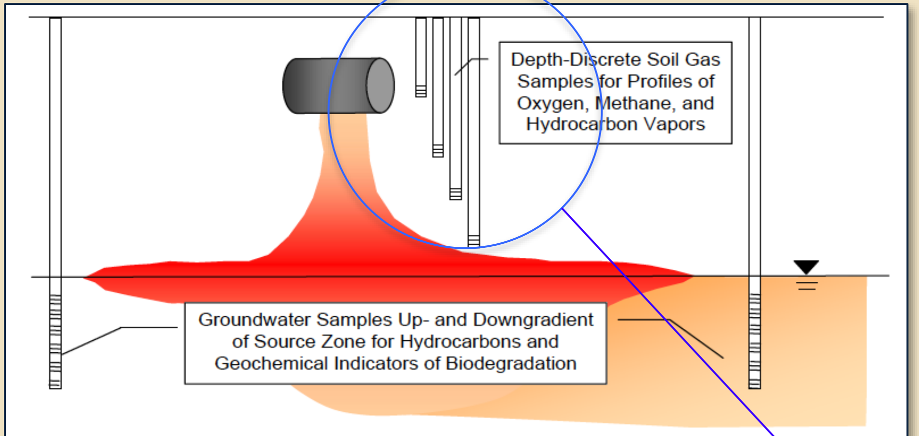
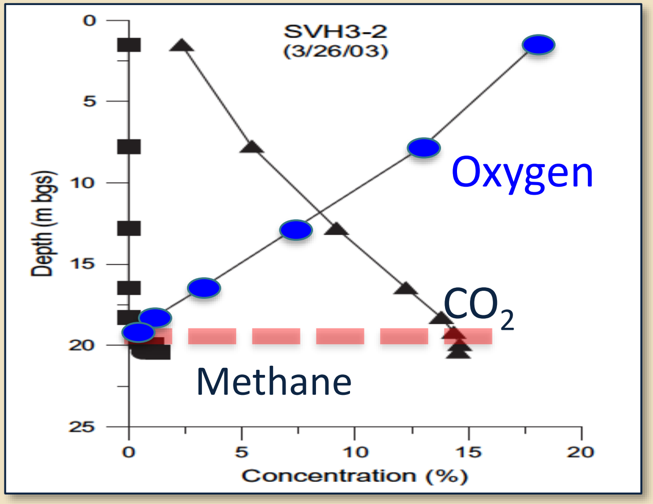


Figure 3-1. Data for qualitative assessment of NSZD.



Lundegard and Johnson, 2006

MEASURING NSZD: C. THERMAL NSZD

+

+

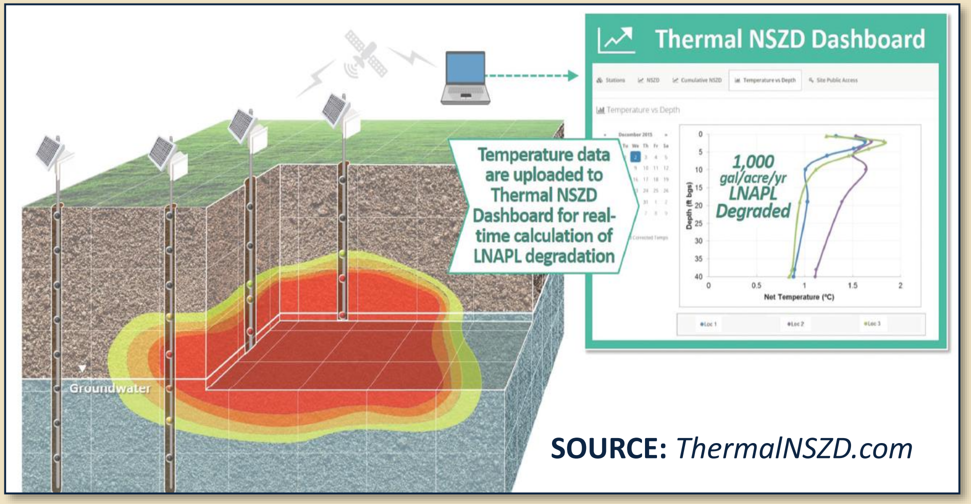
=

Thermocouple on temperature monitoring "stick."

Installation of stick either 1) directly into soil; or 2) into existing monitoring well

Solar power supply and weatherproof box with data logger and wireless communications system.

Thermal NSZD Dashboard Web Page with Daily NSZD Rates



SOURCE: *ThermalNSZD.com*

NSZD RATES BEING OBSERVED

NSZD Study	Site-wide NSZD Rate (gallons/ acre /year)
Six refinery & terminal sites (McCoy et al., 2012)	2,100 – 7,700
1979 Crude Oil Spill (Bemidji) (Sihota et al., 2011)	1,600
Two Refinery/Terminal Sites (LA LNAPL Wkgrp, 2015)	1,100 – 1,700
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100
Eleven Sites, 550 measurements (Palaia, 2016)	300 – 5,600

KEY POINT

NSZD rates are in the range of 100s to 1000s of gallons/acre/year

Source: Garg et al., 2018

EQUIVALENT LNAPL DEGRADATION RATE IN OTHER METHANOGEN-DOMINATED SYSTEMS

Anaerobic Digesters

500,000

Ethanol Release Sites

20,000

Landfills

10,000

Degradation Rate
gal/acre/year

Petroleum Sites

2,000

Wetlands

200

Peat

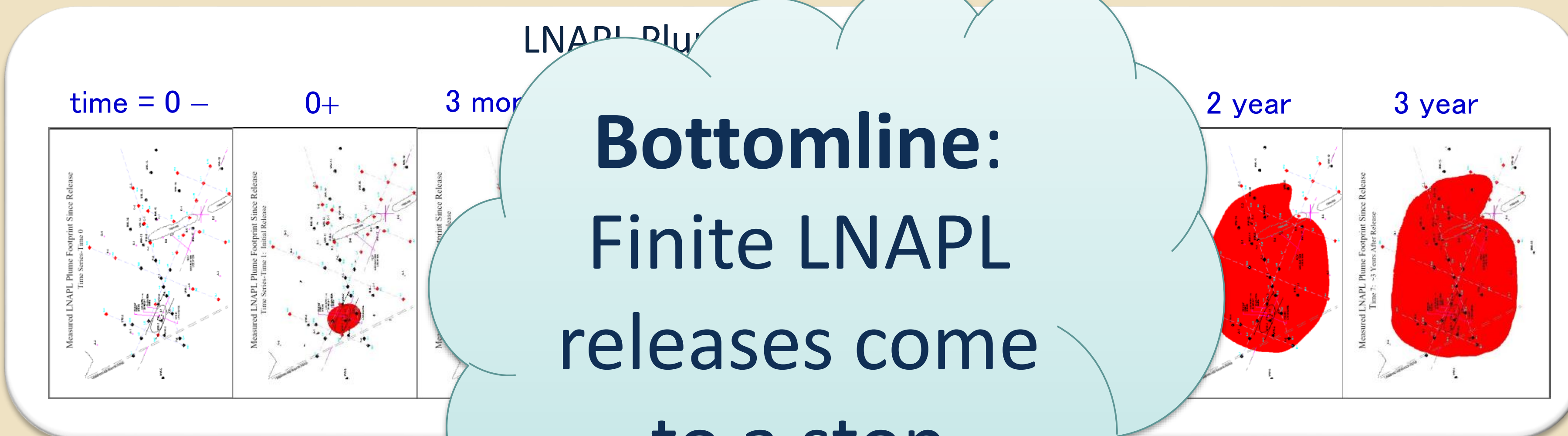
4

Source: Garg et al., 2018

3. LNAPL Bodies Tend to Quickly Reach Equilibrium Once the Release Stops (NSZD Facilitated)

LNAPL Migration

Large volume release on known date from a crude oil pipeline



Bottomline: Finite LNAPL releases come to a stop

- High LNAPL saturation an… …lt in 'fast' initial velocity
- Low saturation & flat LNAPL gradient result in slowing down of the LNAPL plume and pore-entry pressure results in ultimate stoppage of the plume

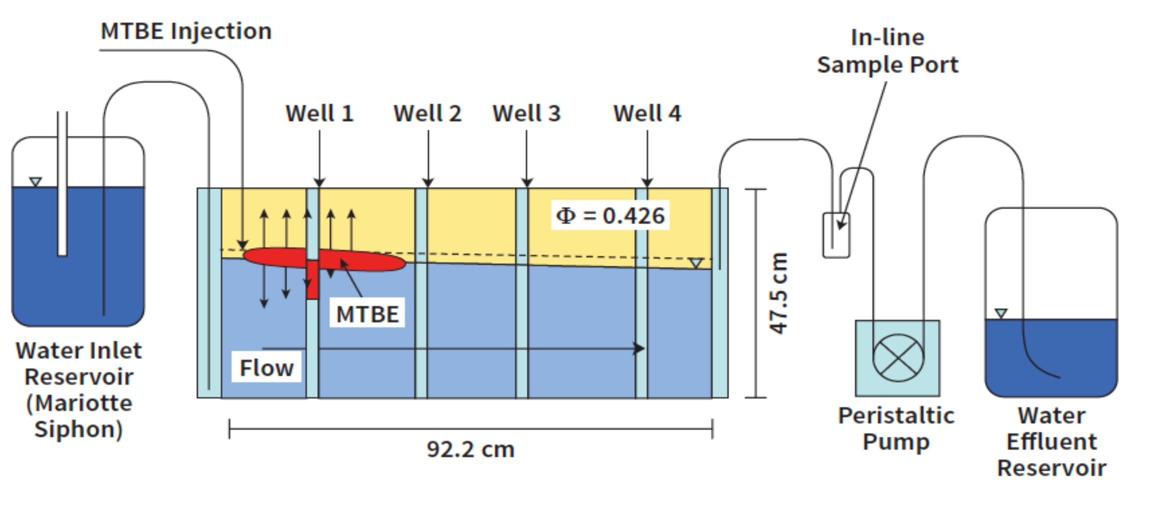
Data from API Interactive LNAPL Guide

3. This is Due to Three Factors:

1) LNAPL Retention in Soil ("sponge effect"), Reduced LNAPL Gradient and 3) NSZD

Modification to LNAPL stabilization conceptual model: *NSZD helps stabilize LNAPL bodies*

In more detail, Mahler et al. (2012a) describes a proof-of-concept experiment where an LNAPL, methyl tert-butyl ether (MTBE), was released into glass-walled sand tanks at a set of step-wise increased release rates. For each continuous release rate, the length of the LNAPL body initially increased and then stabilized. Even under conditions of continuing release of LNAPL into the system and with LNAPL migration within the LNAPL body, the extent of the LNAPL body became stable when losses of the LNAPL through dissolution and volatilization were equal to the rates of LNAPL releases.



Proof of concept LNAPL stability laboratory study – Mahler et al. 2012a

groundwater

A Mass Balance Approach to Resolving LNAPL Stability

by Nicholas Mahler[1], Tom Sale[2], and Mark Lyverse[3]

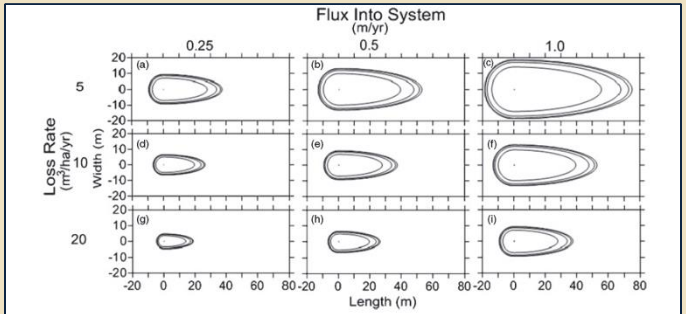
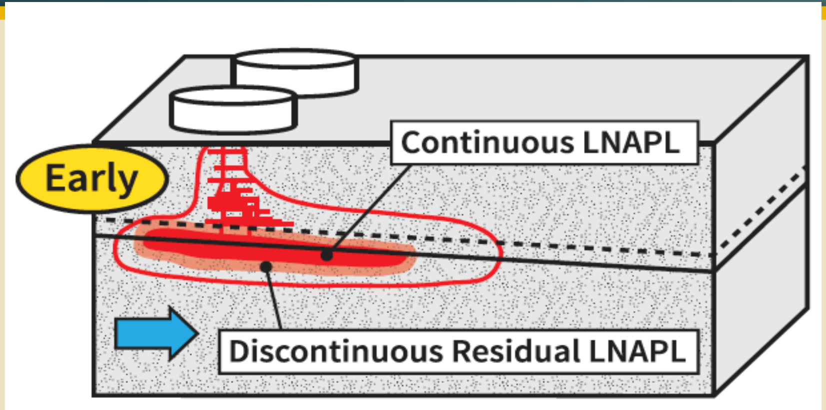


Figure 9. Comparison of the effects of inflow rate and loss rates on the extent over time of an oblong LNAPL body. The contours are given in years. The contour time increments are 40 years for panels (a), (b), and (c), 20 years for panels (d), (e), and (f), and 10 years for panels (g), (h), and (i).

LNAPL FAQ. Sale, Hopkins, Kirkman, 2018

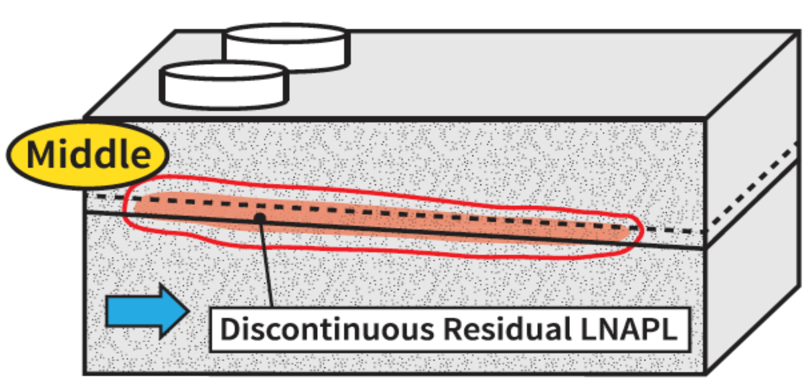
4. Most or Almost all LNAPL Bodies From Historic Releases (more than a decade old) are Likely Stable or Shrinking

Current LNAPL Conceptual Model



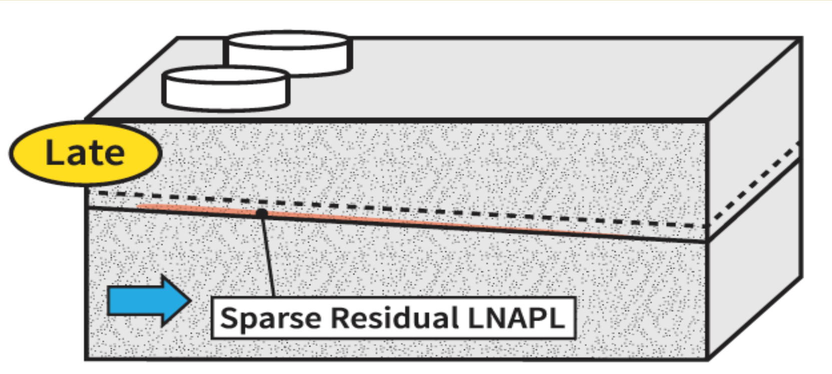
LNAPL expands:

Rare today



LNAPL stable:

More common



Trapped residual LNAPL:

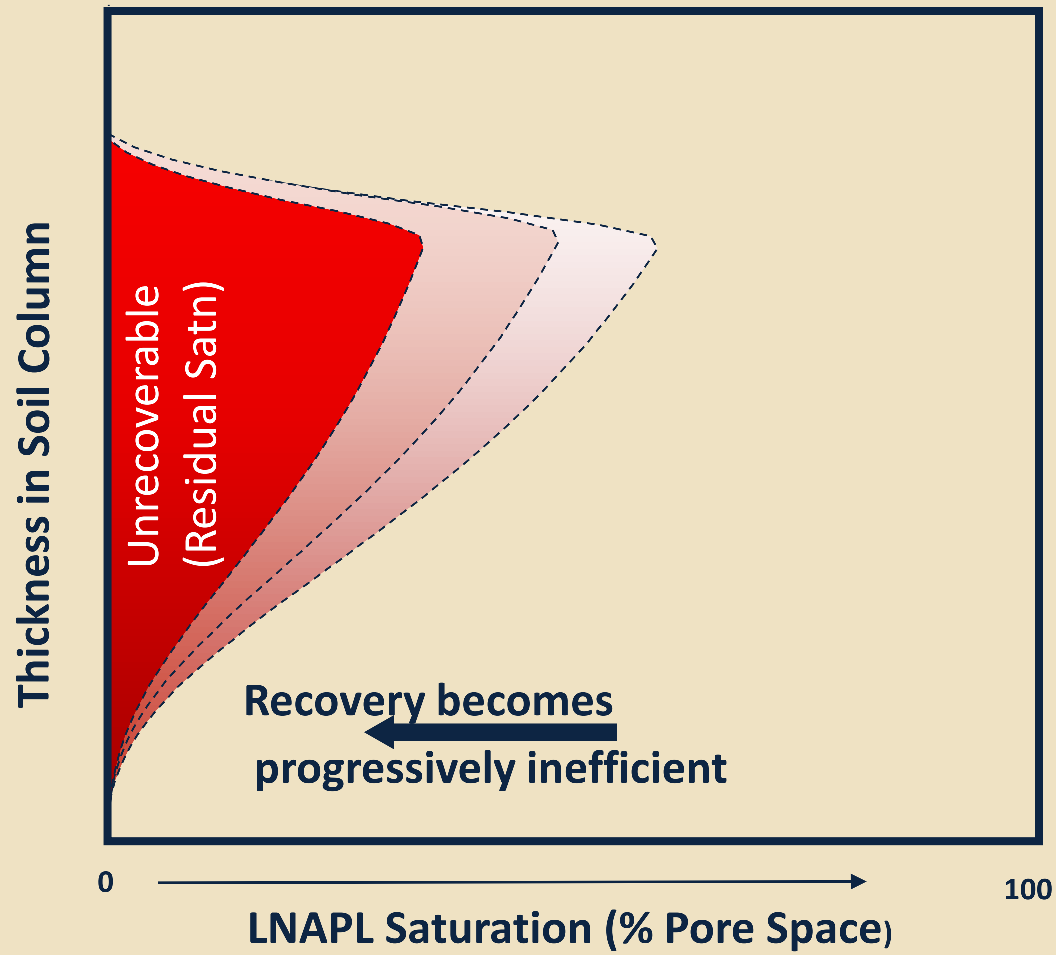
Very common today

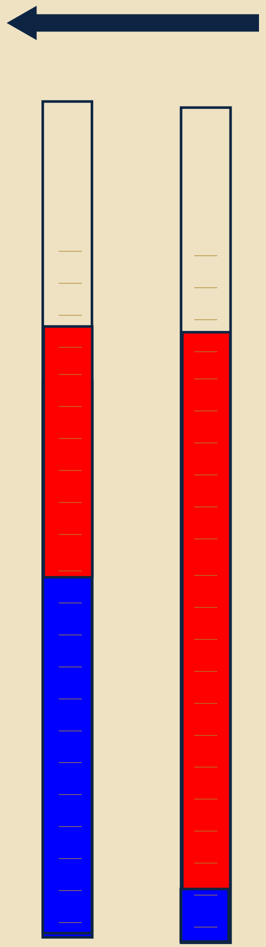
LNAPL FAQ. Sale, Hopkins, Kirkman, 2018

ACTUAL LNAPL CONCEPTUAL MODEL (CONTINUED)

5. Residual LNAPL is immobile due to extremely strong capillary forces in porous media.
6. Residual LNAPL sources typically do not pose a direct risk to receptors.
7. Residual LNAPL source zones transition to “Exhausted LNAPL Sites”, sites with relatively low, stable concentrations of dissolved hydrocarbons in and near the source zone.
8. LNAPL Residual Management Zones are perfect for Late Stage Exhausted LNAPL Sites where there is no risk and where institutional controls can prevent exposure to the LNAPL.
9. Frequent, intense groundwater monitoring does not provide any tangible benefits at Exhausted Sites.

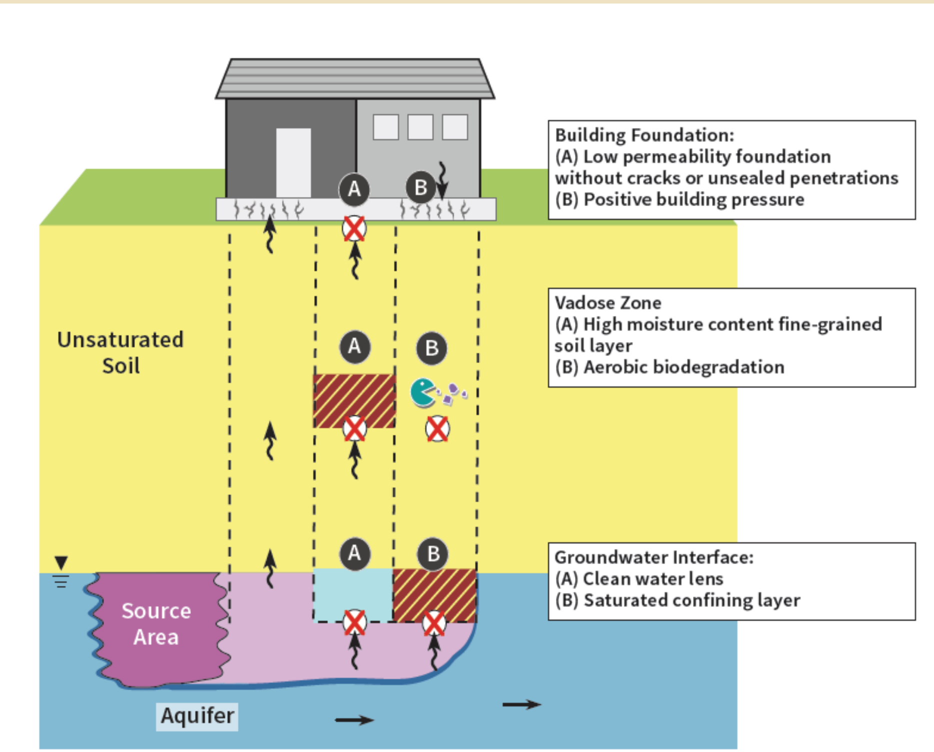
5. Residual LNAPL is Immobile Due to Extremely Strong Capillary Forces in Porous Media.





6. **Residual** LNAPL Sources Typically Do Not Pose a Direct Risk to Receptors.

ITRC Petroleum Vapor Guidance, 2014



LNAPL FAQ. Sale, Hopkins, Kirkman, 2018

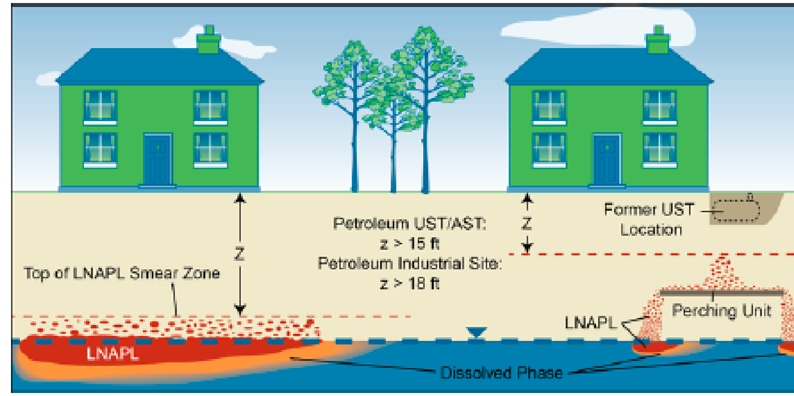


Figure 3-5. Vertical screening distances for LNAPL source.

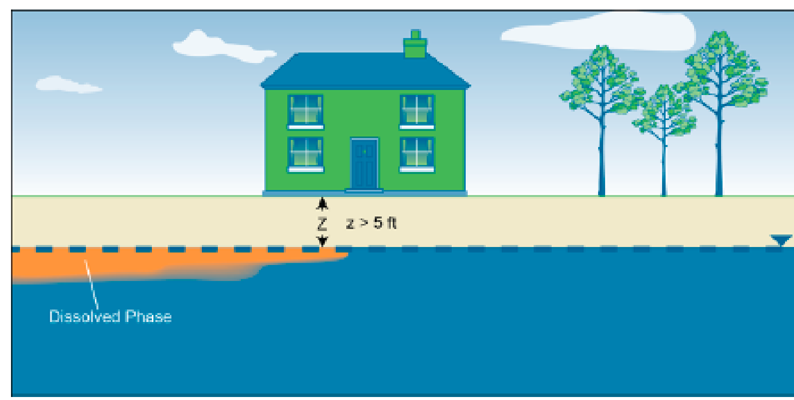


Figure 3-6. Vertical screening distances for dissolved-phase source.

Rapid biodegradation of petroleum vapors means…

You can use screening distances to screen out potential impacts.

EARLY PHASE RELEASES – MOBILE HYDROCARBON REQUIRES PROPER MANAGEMENT

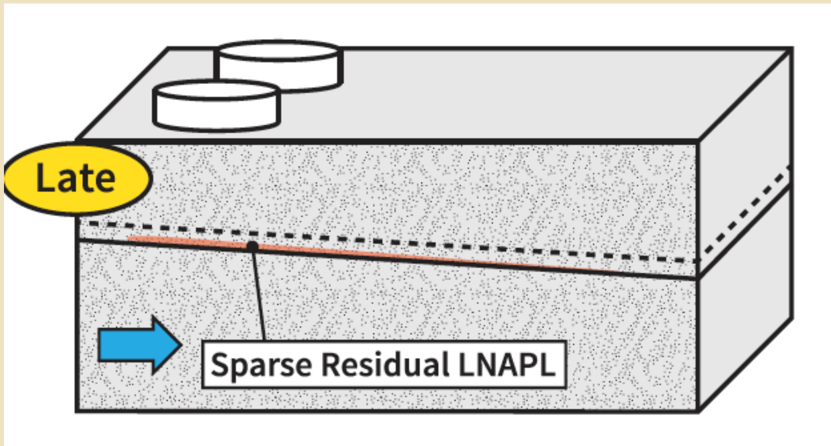
- Ongoing gasoline releases into the sewer system from product pipeline corrosion at the PEMEX terminal
- Improper Initial Response

Results:

- 20 square blocks leveled
- Destroyed over 8km of streets
- 1000's of homes impacted
- Over 200 fatalities
- >1500 people hospitalized
- > 25,000 people evacuated
- Gov't and PEMEX officials arrested

GUADALAJARA, MEXICO – APRIL 1992 EXPLOSIONS

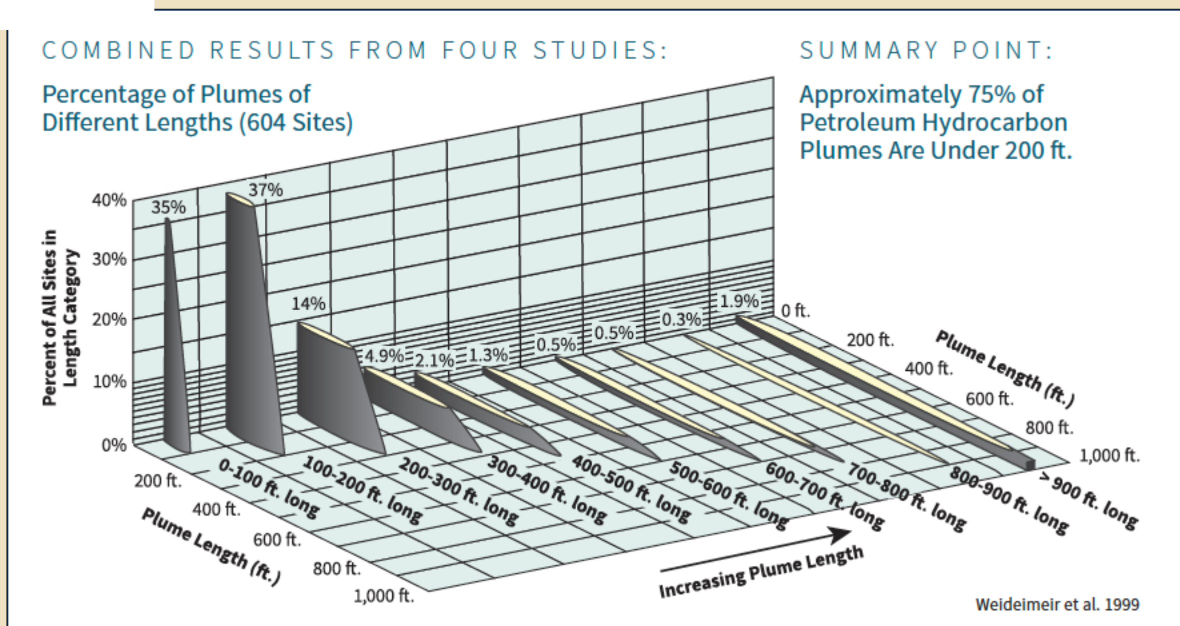
7. Residual LNAPL Source Zones Transition to Late Stage "Exhausted LNAPL Sites",



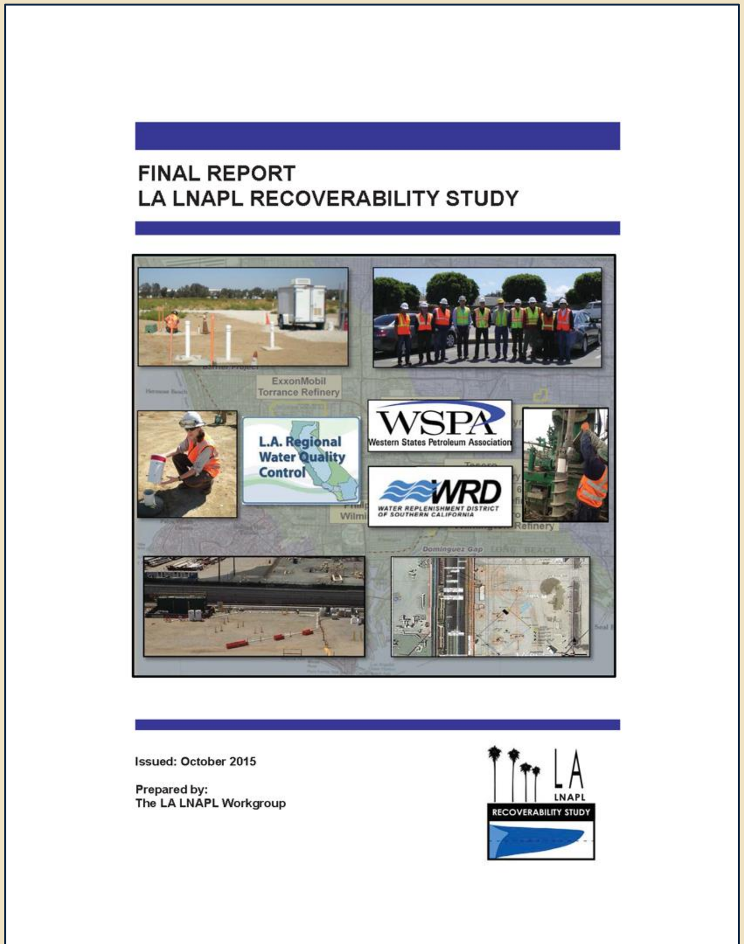
Immobile Residual LNAPL Sources Reduced Over Time by NSZD

Sites with relatively low, stable concentrations of dissolved hydrocarbons in and near the source zone.

Short BTEX Plumes Controlled by MNA



8. LNAPL Residual Management Zones are Perfect for Late Stage Exhausted LNAPL Sites Where There is No Risk and Where Institutional Controls Can Prevent Exposure to the LNAPL.



LA LNAPL Project

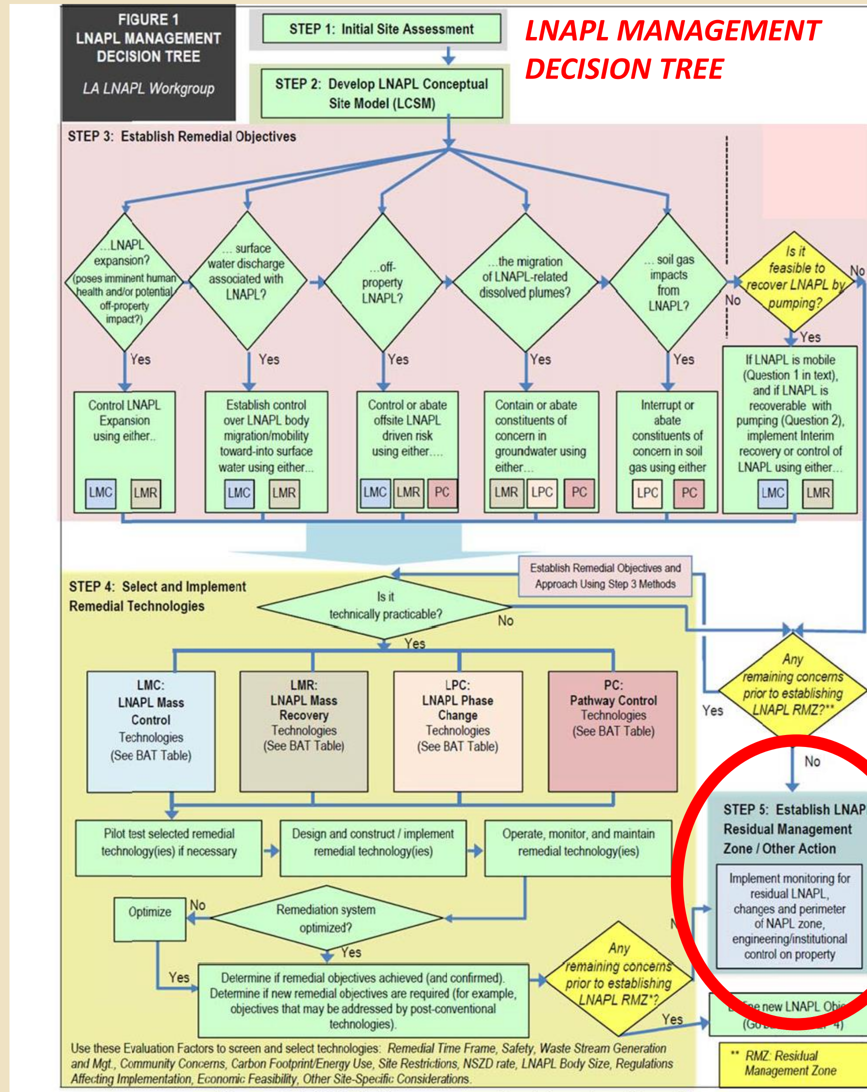


Figure 8.1. LNAPL Management Decision Tree Flow Chart

9. Frequent, Intense Groundwater Monitoring Does Not Provide Any Tangible Benefits at Exhausted Sites.

Groundwater

Time vs. Money: A Quantitative Evaluation of Monitoring Frequency vs. Monitoring Duration

by Thomas E. McHugh[1,2], Poonam R. Kulkarni[2], and Charles J. Newell[2]

- Residual LNAPL zones are very stable.
- No known cases where biodegradation has stopped.
- Doubling the time between monitoring events (e.g., quarterly monitoring to semi-annual monitoring) will reduce costs by 38% will result in no change in the accuracy of the estimated attenuation rate for the same number of events.

Table 2
Trade-Off Between Monitoring Frequency and Monitoring Time for Example Site 1

Monitoring Frequency	Time Required to Characterize Long-Term Attenuation Rate (Years)	Relative Cost to Characterize Long-Term Attenuation Rate
Weekly	1.6	5.3
Twice Monthly	2.1	3.1
Monthly	2.7	2.0
Quarterly	**4.0**	**1**
Semiannual	5.0	0.63
Annual	6	0.39
Every 2 Years	8	0.24

Note: The bold values indicate the baseline monitoring frequency for the example site. Cost is assumed to be proportional to the relative total number of monitoring events required (i.e., the cost of each monitoring event is assumed to be the same regardless of monitoring frequency).

WRAP UP

1. LNAPL apparent thickness in wells ≠ risk
2. LNAPL attenuates much more quickly than once thought due to NSZD
3. LNAPL plumes reach a state of residual saturation once the release stops more quickly due in part to NSZD.
4. Most or almost all LNAPL bodies more than a decade old are likely stable or shrinking
5. Residual LNAPL is immobile due to extremely strong capillary forces in porous media
6. Residual LNAPL sources typically do not pose a direct risk to receptors.
7. "Exhausted LNAPL Sites" have relatively low, stable plume concentrations
8. LNAPL Residual Management Zones are perfect for Exhausted LNAPL Sites
9. Frequent, intense groundwater monitoring <u>does not</u> improve our understanding of these sites

THANK YOU FOR YOUR KIND ATTENTION

Spare slides