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User Manual for Concawe LNAPL Toolbox

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User Manual for Concawe LNAPL Toolbox

Prepared by:

LNAPL Toolbox:

Strasert, B., C. Newell, P. de Blanc, P. Kulkarni, K. Whitehead, B. Sackmann, and H. Podzorski, 2021. Concawe LNAPL Toolbox, Concawe, Brussels, Belgium.

User Manual:

Newell, C.J., B. Strasert, P. de Blanc, P. Kulkarni, K. Whitehead, B. Sackmann, and H. Podzorski, 2021. User Manual for Concawe LNAPL Toolbox, Concawe, Brussels, Belgium.

At the request of:

Concawe STF-33 Task Force

(Markus Hjort, Eleni Vaiopoulou , Brnada Angelika, Mónica Castro, Patrick Eyraud, Richard Gill, Tim Greaves, Thomas Grosjen, Christelle Jennet, Wayne Jones, Jose Miguel Martinez Carmona, Andras Medve, Jonathan Smith)

ABSTRACT

The Concawe LNAPL Toolbox is a wide-ranging but easy to use web-based toolbox to deliver key LNAPL knowledge to the LNAPL remediation community. The toolbox uses a three-tiered approach that provides access to over 20 different LNAPL tools (key infographics, nomographs, calculators, mobility models, videos, checklists, and other formats) with different levels of complexity, activation energy, and time requirements. The three tiers of complexity are:

Tier 1: Simple, Quick Graphics, Tables, Background Information
Tier 2: Middle Level Quantitative Methods, Tools
Tier 3: Gateway to Complex Models

In terms of content, the Concawe LNAPL Toolbox is designed to address six questions via six different sections:

1. How much LNAPL is present?
2. How far will the LNAPL migrate?
3. How long will the LNAPL persist?
4. How will LNAPL risk change over time?
5. Will LNAPL recovery be effective?
6. How can one estimate NSZD?

The Concawe LNAPL Toolbox is designed to be accessed via a webpage on an internet browser (http://lnapltoolbox.concawe.eu/lnapl_toolbox/), or by downloading the toolbox for use on a personal computer.

KEYWORDS

LNAPL, Light Non-Aqueous Phase Liquids, LNAPL transmissivity, Specific Volume, Migration, Persistence, Risk, Recovery, NSZD, Models, Calculators, LDRM, LNAST, dissolution, REMFuel, composition

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.org).

CONTENTS

1. QUICK START

Step 1: Determine the question you would like to learn more about (Column 1).

Step 2: Decide on the level of effort you would like to apply (Columns 2 through 4):

Tier 1: a few minutes

Tier 2: a few hours

Tier 3: learn about more complex tools

Step 3: Go to the appropriate tab using the Home Page buttons or the Navigation Bar.

Key LNAPL Questions	Tier 1 Quick Info	Tier 2 Models / Tools	Tier 3 Gateway to Complex Tools
How much LNAPL is present?	Simple Table and Graphic	New LNAPL Volume / Extent Tool	LDRM Resources and Video
How far will LNAPL migrate?	Simple Graphic	New LNAPL Additional Migration Tool and Mahler Migration Model	HSSM and UTCHEM Resources and Video
How long will LNAPL persist?	Simple Graphic and Table	New LNAPL Lifetime Calculator	LNAST and REMFuel Resources and Videos
How will LNAPL risk change over time?	Simple Tables	New LNAPL Dissolution Calculator	LNAST Resources and Video
Will LNAPL recovery be effective?	Simple Graphics	New LNAPL Transmissivity & Darcy Flux Calculator	Computer Modelling Resources
How can one estimate NSZD?	Simple Graphic	NSZD Rate Converter, NSZD Temperature Enhancement Calculator	NSZD Resources and Videos

The following sections of the User Manual include more detail on each of the 18 tabs above. Each of the 18 sections is designed to be a stand-alone document, so there is some duplication of information in the different sections.

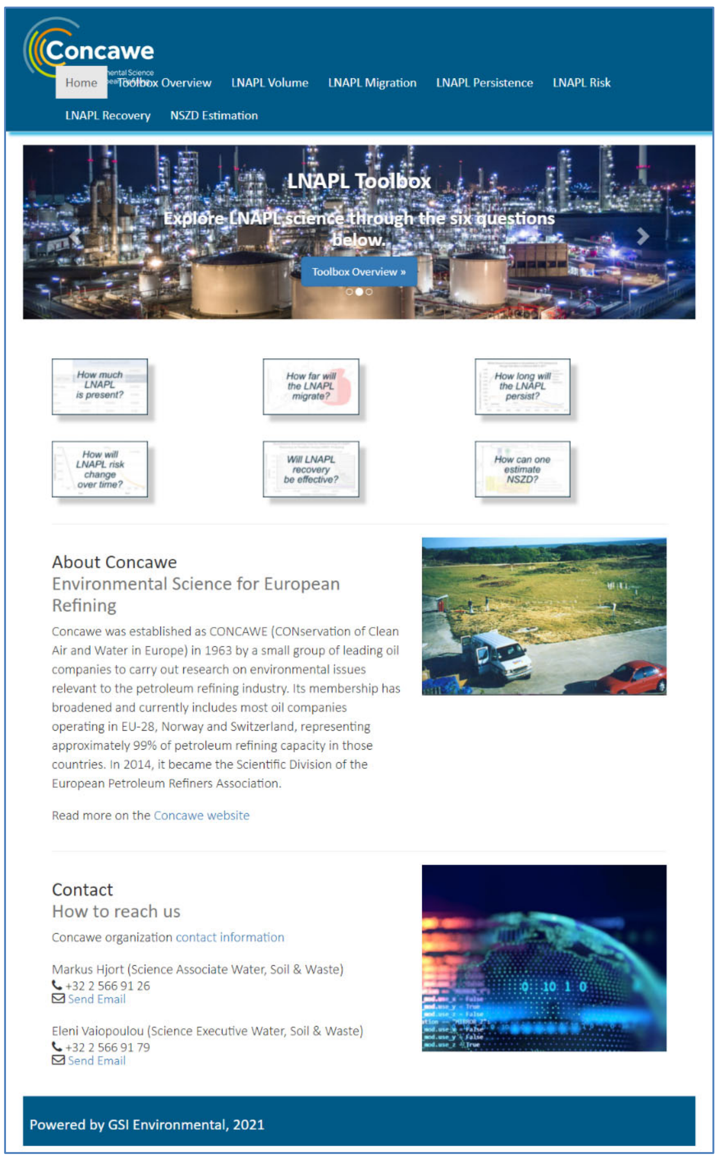
2. HOME PAGE

2.1. WHAT THIS PAGE DOES

This page describes Concawe, the organization that funded the LNAPL Toolbox. It provides two ways to navigate to answer six key questions:

- Method 1: Click on one of the six key LNAPL question buttons below the large image.

- Method 2: Use the tabs near the top of the page to get to an overview of the Toolbox, or to go to one of the sections for the six key LNAPL questions.



3. TOOLBOX OVERVIEW

3.1. WHAT THIS PAGE DOES

Provides overview of the Toolbox via these questions and answers:

1. **What is LNAPL?** LNAPL stands for "Light Non-Aqueous Phase Liquids" or hydrocarbons that exist as a separate undissolved phase in the subsurface at some sites with legacy releases of fuels. They are referred to as "Light" because most petroleum hydrocarbons are less dense than water. Because LNAPLs can sustain groundwater plumes for long time periods, it is important to understand how much LNAPL may be present at site, if the LNAPL can migrate, if it can be recovered, how the LNAPL composition changes over time, how long it may persist, and finally quickly the LNAPL body is attenuating.

2. **What is the Vision Behind the Concawe LNAPL Toolbox?** Concawe envisioned compiling a unique collection of useful tools, calculators, data, and resources to help LNAPL scientists and engineers better understand how to manage LNAPL at their sites.

3. **How is the Toolbox Organized?** It is structured around six key questions:

    1. How much LNAPL is present?
    2. How far will the LNAPL migrate?
    3. How long will the LNAPL persist?
    4. How will LNAPL risk change over time?
    5. Will LNAPL recovery be effective?
    6. How can one estimate NSZD?

    ….with each question being addressed via three Tiers of complexity:

    1. Tier 1: Simple, Quick Graphics, Tables, Background Information

2. Tier 2: Middle Level Quantitative Methods, Tools

3. Tier 3: Gateway to Complex Models

4. How Do I Use the Toolbox?

1. Option 1: Run the Toolbox by accessing the webpage on an internet browser. Recommended browsers: Google Chrome, Mozilla Firefox, and Safari

2. Option 2: Download the Toolbox for use on your own computer or server. Required software: R > 4.0.2 and Python > 3.8

5. Who Developed the Toolbox?

See text box to right.

Concawe Soil Groundwater Taskforce (STF-33)	GSI Environmental Team
Markus Hjort, MSc	Brian Strasert, P.E.
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Tim Greaves	Poonam Kulkarni, P.E.
Wayne Jones	Kenia Whitehead, Ph.D.
Thomas Grosjean	Brandon Sackmann, Ph.D.
Andrew Kirkman	Hannah Podzorski
Jonathan Smith, Prof.	
Richard Gill, PhD.	
Jose Miguél Martinez Carmona	
Peter Discart	

6. How Do I Cite the Concawe LNAPL Toolbox?

Strasert, B., C. Newell, P. de Blanc, P. Kulkarni, K. Whitehead, B. Sackmann, and H. Podzorski, 2021. Concawe LNAPL Toolbox, Concawe, Brussels, Belgium.

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4. HOW MUCH LNAPL IS PRESENT?

There are three levels of information that are delivered with the Concawe LNAPL Toolbox:

- Tier 1: Simple, Quick Graphics, Tables, Background Information
- Tier 2: Middle Level Quantitative Methods, Tools
- Tier 3: Gateway to Complex Models

Each of the three Tiers are described below in this Section.

4.1. TIER 1 QUICK INFO: HOW MUCH LNAPL IS PRESENT?

4.1.1. Introduction: Specific Volume

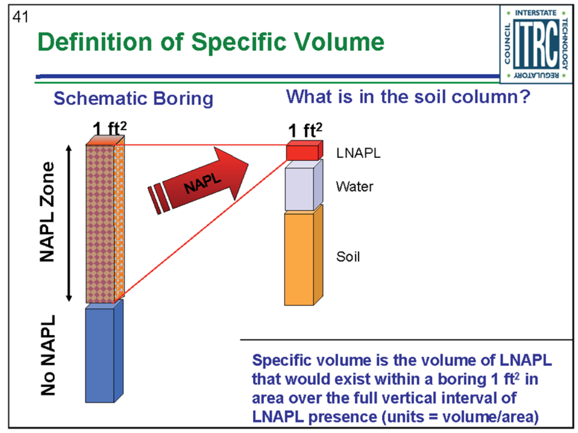
In the past, a common misconception of the vertical distribution of free product at the water table was based on the idea that LNAPL occurs as a distinct lens in which the drainable pore space is completely saturated with LNAPL and that the thickness of LNAPL monitoring well accurately represented the thickness of LNAPL in the formation. This was often referred to as the "pancake layer" model for LNAPL, but it does not reflect the important part soil properties play in the relationship between the amount of LNAPL in the formation and the thickness of LNAPL in a well (referred to as "apparent thickness").

	If a well has this much LNAPL:		
	0.1 metre	0.3 metre	1 metre
Soil Type	This much LNAPL is in the formation (m^3/m^2):		
Silty Clay	0.000041	0.00039	0.0045
Silt	0.00020	0.0028	0.040
Loam	0.00034	0.0058	0.084
Sand	0.0025	0.059	0.32

Table developed for Concawe Toolbox 2020 using LNAPL tool developed by de Blanc, P. and S. K. Farhat, 2018. 25th IPEC: International Petroleum Environmental Conference October 30 – November 1, 2018. Denver, Colorado.

In the table to the right, the amount of LNAPL in the formation for three different apparent LNAPL thicknesses in a monitoring well is described in terms of a "specific volume." The specific volume is the volume of LNAPL in a given location divided by the surface area. This is a calculated value of the actual amount of LNAPL present in an area divided by the area. This would be the thickness of LNAPL that would remain in an LNAPL zone if the soil and water in that area were hypothetically removed.

For example, if there is one metre of LNAPL measured in a monitoring well screened in a sand, that corresponds to about 0.32 cubic metres (320 litres) of LNAPL per square metre of area. If this well was screened in a silt, there would only be about 0.040 cubic metres (40 litres) of LNAPL per square metre of area. This table shows the relationship between soil type, apparent LNAPL thickness, and the actual amount of LNAPL in the formation per square metre of area. The figure to the right shows how the ITRC LNAPL Training Course describes LNAPL Specific Volume.



Source: ITRC LNAPL Training

There are two types of specific volume:

Specific Volume: All the LNAPL present in the subsurface is used;

Mobile Specific Volume: Only the LNAPL present above the LNAPL residual saturation is used.

4.2. TIER 2 MODELS/TOOLS: HOW MUCH LNAPL IS PRESENT?

4.2.1. Multi-site LNAPL Volume and Extent Model (de Blanc and Farhat, 2018)

A new tool to determine the volume of subsurface LNAPL has been created. The tool is an extension of the commonly used LNAPL Distribution and Recovery Model (LDRM) developed for the American Petroleum Institute (API) by Dr. Randall Charbeneau of the University of Texas (Charbeneau, 2007). The new tool accommodates multiple soil layers, multiple locations, a highly accurate integration method, and automatic interpolation.

LDRM is frequently used to determine the subsurface LNAPL specific volume (volume per unit area, Do) and transmissivity (Tn). Point estimates of Do can then be used to determine subsurface LNAPL volumes, and Tn estimates can be used to optimize remediation.

LDRM calculates Do and Tn at a single location based on user input for up to three soil layers. Although LDRM is widely used by practitioners, a limitation of the software is the need develop a separate input file to calculate LNAPL Do and Tn at each location where LNAPL apparent thickness has been measured. These limitations can make determinations of Do and Tn time-consuming and expensive when many measurements are needed.

The Multi-site tool was developed to overcome some of the limitations of LDRM. The tool calculates Do and Tn at an arbitrary number of locations for up to ten different soil layers of differing lithology. Any number of soil types and properties may be specified by the user. The simultaneous determinations of Do and Tn at many locations saves a tremendous amount of time when many locations must be analysed. Do and Tn are calculated in the same manner as in LDRM.

LNAPL Do and Tn can be calculated by integrating LNAPL saturations over the thickness of LNAPL in the formation. A total LNAPL volume is estimated as an area-weighted average of these calculated thicknesses.

4.2.2. Details of the Multi-site LNAPL Volume and Extent Model

4.2.2.1. What the Model Does

The Multi-site tool calculates several key LNAPL values, including specific volume, recoverable volume, and transmissivity, at multiple locations for multiple layers of differing soil types. These values are used to calculate a total subsurface LNAPL volume. Based on LNAPL gradients specified by the user, estimated LNAPL velocities are also calculated. The distribution of calculated values is depicted graphically.

4.2.2.2. How the Model Works

The model is based on an extension of the methodology of the API's LDRM (Charbeneau, 2007). The user enters data into three different input databases: 1) a soil parameter input database, 2) a well coordinate and fluid level gauging input database, and 3) a stratigraphy input database. The model determines the layers in which LNAPL is present, then calculates specific volume and other LNAPL parameters for the layered system. An area-weighted average of the specific volume is calculated to arrive at a total LNAPL volume.

4.2.2.3. Key Assumptions

The model assumes that the LNAPL is in hydrostatic equilibrium with the surrounding media. Relative permeability is calculated by combining the Mualum model with the van Genuchten soil characteristic curve parameters (Charbeneau, 2007). See the attachment "Soil Properties Resources" for more details about how to convert between different soil classification systems.

4.2.3. Steps for Using the LNAPL Volume and Extent Model

1. Download the data template.

	A	B	C	D	E	F	G
1	Monitoring Well	Date	Latitude	Longitude	LNAPL Top Depth Below Ground Surface (m)	LNAPL Bottom Depth Below Ground Surface (m)	LNAPL Gradient (m/m)
2	TF-01	2009-06-25	53.4792235	-31.6370004	6.03	6.03	0.0086
3	TF-02	2009-06-25	53.4787581	-31.6367291	6.46	6.46	0.0086
4	TF-03	2009-06-25	53.4788652	-31.6367142	6.44	6.45	0.0086

2. On the "Location_Information" tab, enter the following information for each location where you have LNAPL thickness data in a monitoring well:

Latitude, Longitude in decimal degrees (if you do not have latitude and longitude, you must geo-reference one of your existing figures using a GIS system or commission surveyors to obtain these data). You will need to have latitude and longitude data that is to the 5th decimal place (0.00001 decimal degrees) to get locations within one metre accuracy.

Top and Bottom Depth of LNAPL Below Ground Surface: Calculations of LNAPL properties like Do and Tn are independent of elevation and only rely on lining up the stratigraphy with the LNAPL measurements at each location. Units: metres.

LNAPL Gradient: The change in vertical top of LNAPL elevation between two monitoring points in the area of the LNAPL observation divided by the distance between these points. Do not use elevations corrected for LNAPL / water density effects. The gradient is entered by the user and not calculated by the tool, so elevation differences between points do not matter. Units: metre per metre.

Use as many rows as you have locations for your site.

3. On the "Stratigraphy" tab, enter the *Soil Type* for each layer in each monitoring well. You are limited to one of the soil types shown on the "Soil_Types" tab (you can copy and paste the soil type from "Soil_Types" to "Stratigraphy", although, as explained in the next section, you can customize the soil type list). The default soil types are from Carsel and Parrish (1988). Enter the *Depth* to the top of that layer in metres and the *Depth* to the bottom of that layer in metres.

	A	B	C	D
1	Monitoring Well	Layer Top Depth Below Ground Surface (m)	Layer Bottom Depth Below Ground Surface (m)	Soil Type
2	TF-01	2.44	3.66	Clay
3	TF-01	3.66	6.40	Silt
4	TF-01	6.40	7.01	Loamy sand
5	TF-01	7.01	8.54	Silt loam
6	TF-01	8.54	10.98	Silty clay
7	TF-01	10.98	12.80	Sand
8	TF-01	12.80	13.11	Clay
9	TF-02	2.44	3.05	Clay
10	TF-02	3.05	4.27	Silt
11	TF-02	4.27	4.88	Loamy sand
12	TF-02	4.88	7.93	Silt loam
13	TF-02	7.93	13.11	Silty clay
14	TF-02	13.11	14.94	Sand
15	TF-02	14.94	15.24	Clay
16	TF-03	3.66	5.18	Clay
17	TF-03	5.18	5.79	Silt
18	TF-03	5.79	7.01	Loamy sand
19	TF-03	7.01	8.84	Silt loam
20	TF-03	8.84	15.55	Silty clay
21	TF-03	15.55	19.21	Sand
22	TF-03	19.21	19.51	Clay
23	TF-04	2.44	3.35	Clay
24	TF-04	3.35	4.27	Silt
25	TF-04	4.27	5.79	Loamy sand

4. You can replace any of the data on the "Soil_Types" tab with site-specific data or a custom soil type.

Porosity is the effective porosity of the soil (replace with lab measurements or your preferred estimated effective porosity). Units: unitless.

Ks is the saturated hydraulic conductivity for water flowing in the soil in units of metres per day. Users can use the default values for each soil provided in the data input spreadsheet, or they can replace these estimated values with data from slug tests or pumping tests other preferred values for Ks. Units: metres per day.

	A	B	C	D	E	F	G	H
1	Soil types 1 through 12 from Carsel and Parrish (1988)					van Genuchten Parameters		
2	Soil Num	Soil_Type	Porosity	Ks (m/d)	Theta_wr	N	alpha (1/m)	M
3	1	Clay	0.38	0.048	0.068	1.09	0.8	0.08
4	2	Clay loam	0.41	0.062	0.095	1.31	1.9	0.24
5	3	Loam	0.43	0.25	0.078	1.56	3.6	0.36
6	4	Loamy sand	0.41	3.5	0.057	2.28	12.4	0.56
7	5	Silt	0.46	0.06	0.034	1.37	1.6	0.27
8	6	Silt loam	0.45	0.11	0.067	1.41	2	0.29
9	7	Silty clay	0.36	0.0048	0.07	1.09	0.5	0.08
10	8	Silty clay loam	0.43	0.017	0.089	1.23	1	0.19
11	9	Sand	0.43	7.1	0.045	2.68	14.5	0.63
12	10	Sandy clay	0.38	0.029	0.1	1.23	2.7	0.19
13	11	Sandy clay loam	0.39	0.31	0.1	1.48	5.9	0.32
14	12	Sandy loam	0.41	1.1	0.065	1.89	7.5	0.47
15	*Add additional rows as needed.*							

The soil type table is based on the USDA soil classification system. If your soil data are classified using the USCS system, you can convert to the USDA soil type using the table below (Garcia-Gaines and Frankenstein, 2015) (supporting data are shaded). See the attachment "Soil Properties Resources" for more details.

Table 17. Consensus of the most probable (MP) and possible (P) USCS classification per USDA texture classification.

	USCS classification						
	SSURGO (2014) *Table 8* WES (1961) *Table 9* Wilson et al. (1965) *Table 10* Rollings and Rollings (1996) *Table 11* Curtis (2005) *Table 12*		Ayers et al. (2011) *Table 13*		Baylot et al. (2013) *Table 14*	FASST (2004) *Table 15*	
USDA Classification	**MP**	**P**	**MP**	**P**	**MP**	**MP**	**Consensus**
Sand	SM	SP-SM	SW, SP	–	SP	SP	SP
Loamy Sand	SM	CL	SM	SC	SM	SM	SM
Sandy Loam	SM	ML, CL	SM	–	SC	SM	SM
Sandy Clay Loam	CL	SC	SC	–	SC	SC	SC
Sandy Clay	SC, CL	–	SC	CL	SC	SC	SC,
Loam	CL	ML	ML	–	CL	ML	CL
Silt Loam	CL	ML	ML	–	SM	ML	ML
Silt	ML	–	ML	–	ML	ML	ML
Clay Loam	CL	–	CL, MH	–	CL	CL	CL
Silty Clay Loam	CL	ML, CH	MH	–	CL	CL	CL
Clay	CH, CL	GC	CH	CL	CH	CH	CH
Silty Clay	CH, CL	–	CL, MH	–	CL	CH	CH

5. In the “Choose Input File” section in the tool, select “Browse” to upload the file.

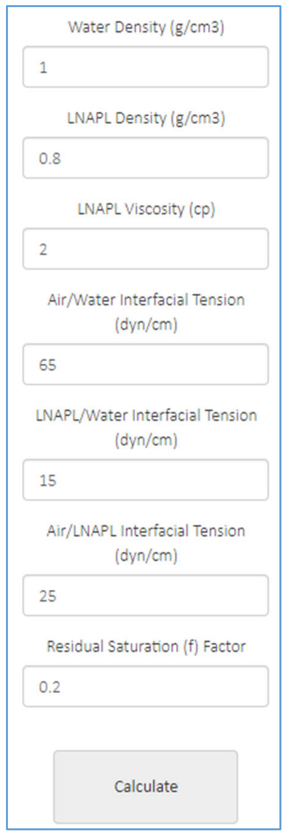
Enter data for the following parameters on the input screen itself:

Water Density: Typically enter 1 g/cm^3 unless the groundwater is saline. You usually do not need to make a correction for temperature because temperature has a small effect on water density. Units: grams per cubic centimetre.

LNAPL Density, LNAPL Viscosity, LNAPL/Water Interfacial Tension: Use values from the table below from page 10 of Source Report A of the LA LNAPL Recoverability Study (link below) or enter values from laboratory tests of your LNAPL.

https://www.gsi-net.com/en/publications/la-lnapl-recoverability-study.html

	Density @ 15°C (g/cm^3)	Viscosity (cp)	Interfacial Tension (dynes per cm)
Gasoline	0.729	0.355 – 0.659	50
Diesel	0.827	Wide range	4 - 28.2
JP A/B	0.77 – 0.79	1.18 -1.59	50 (API 4729)
Crude Oil	0.832 – 0.914	Wide range	25-30.5



Units for density: grams per cubic centimetre.

Units for viscosity: centipoise.

If you are considering performing laboratory tests to measure your LNAPL properties, the API document Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models is a useful compilation of testing methods.

https://www.api.org/oil-and-natural-gas/environment/clean-water/groundwater/lnapl/~/media/97D9B7561D34477F85D790DC1E3CCDBB.ashx

Air/Water Interfacial Tension (surface tension): 65 dyn/cm is typically used for fresh groundwater. Units: dynes per centimetre.

Air/LNAPL Interfacial Tension: These data are typically not measured but estimated. A value of 25 dyne/cm is often used. Units: dynes per centimetre.

Residual Saturation (f) Factor: The f factor is described in the text box to the right (page 46 of Source Report A of the LA LNAPL Recoverability Study. Units: unitless.

4. F-Factor method. Charbeneau (2007) and Johnson and Adamski (2005) present a model for estimation of residual LNAPL saturation based on the maximum LNAPL saturation experienced by the soil (the "initial" LNAPL saturation). The model assumes that the residual saturation is linearly related to the initial saturation by:

$$S_{or} = f_r S_{oi} \qquad \text{Equation 4.8}$$

where: S_{or} = LNAPL residual saturation (L^3 LNAPL/L^3 pores);
f_r = residual f-factor (unitless); and,
S_{oi} = initial LNAPL saturation (or maximum LNAPL saturation at any time; L^3 LNAPL/L^3 pores)

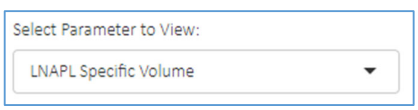
The residual f-factor appears to vary with soil texture and may also be different for saturated and unsaturated soils (Charbeneau, 2007). Vadose zone values of the f-factor determined using a similar model are reported to be 0.2 to 0.5, with a median value of 0.3 (Charbeneau, 2007). Charbeneau (2007) also reports on laboratory work by other researchers on specific soils and fresh LNAPL that give the following residual f-factor values:

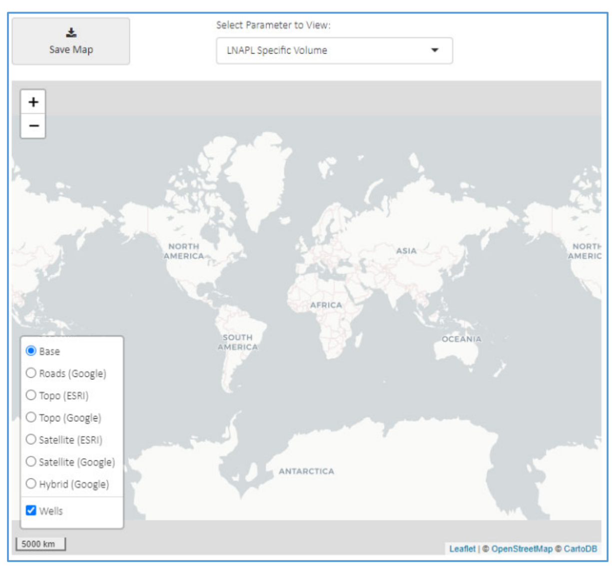
Soil Type	factor values
Ottawa sand	0.18
Fine to medium sand (Safety Bay)	0.23
Fine sand and loamy sand (Texas City)	0.39 and 0.43
Clay loam (Swan Valley)	0.56

6. Use the map search/selection tool to build a *base map* for the graphical display of the LNAPL spatial information (see selection options to the right).

7. Click the "Calculate" button in the bottom / middle of the input screen.

Select one of the following Output Parameters to view on the map:





LNAPL Specific Volume: See Section 4.1.1 for an overview of specific volume. Units: cubic metres of LNAPL per square metre of horizontal surface area. (This unit is equivalent to metres of LNAPL).

Recoverable LNAPL Specific Volume: See Section 4.1.1 for an overview of specific volume. Units: cubic metres of LNAPL per square metre of horizontal surface area. (This unit is equivalent to metres of LNAPL).

Average LNAPL Relative Permeability: Relative permeability is a concept used to convey the reduction in fluid flow caused by the presence of multiple mobile fluids. It is the ratio of the hydraulic conductivity of the fluid at a given saturation to the fluid hydraulic conductivity at complete saturation with the fluid of interest. Units: unitless.

Maximum Thickness of Free LNAPL: The vertical thickness of formation surrounding a well that contains LNAPL at any saturation. Units: metres.

Average LNAPL Hydraulic Conductivity: The average hydraulic conductivity of the LNAPL, obtained using the saturated water hydraulic conductivity corrected for relative permeability and LNAPL density and viscosity. Units: metres per day.

Average Transmissivity: The average transmissivity of the LNAPL for all the data points. It is often compared to an LNAPL transmissivity threshold to determine if the LNAPL is likely to be recoverable using conventional technologies such as LNAPL skimming or pumping (see Section 8.2 or the short excerpt below):

Based on guidance from ITRC (2018), the key threshold for LNAPL recovery is the LNAPL transmissivity has to be higher than this general range of numbers: 0.0093 to 0.074 m2/day. The range should be interpreted as a grey area for recoverability. If the calculated or measured LNAPL transmissivity is below that the lowest value, then there is a high probability that LNAPL hydraulic recovery will not to be cost effective or efficient. If above the highest number, then hydraulic recovery has a much higher likelihood of being feasible.

LNAPL Unit Flux: The volume of LNAPL that is passing through a unit width of the porous medium per unit area per day. Units: cubic metres per metre per day.

Average LNAPL Seepage Velocity: The calculated average velocity of LNAPL through the water bearing unit. This is likely a conservative value as losses due to Natural Source Zone Depletion (NSZD) are not considered (see Section 9.0). Units: metres per day.

8. You can save the map for later by clicking the "Save Map" button.

9. Click the tab for "Interpolation" will show an interpolation of the distribution of the selected parameter across the site, along with the Area-Weighted Specific Volume and Recoverable Specific Volume.

4.2.3.1. Developers

This LNAPL tool, sometimes referred to as the LNAPL Volume and Extent Model, was developed by **Dr. Phillip de Blanc and Dr. Shahla Farhat** of GSI Environmental, Houston, Texas. Reference this way:

de Blanc, P.C., and S. K. Farhat, 2020. LNAPL Volume and Extent Model. Programmed by GSI Environmental for the Concawe LNAPL Toolbox.

4.2.3.2. References

Carsel, R.F., and R.S. Parrish. 1988. Developing joint probability distributions of soil water retention characteristics. Water Resour. Res. 24:755-769.

Charbeneau, 2007. LNAPL Distribution and Recovery Model (LDRM) Volume 1: Distribution and Recovery of Petroleum Hydrocarbon Liquids in Porous Media, Randall J. Charbeneau, American Petroleum Institute.de Blanc, P.C., and S. K. Farhat. 2018. New Tool for Determining LNAPL Volume and Extent. 25TH IPEC:

International Petroleum Environmental Conference October 30 – November 1, 2018 * Denver, Colorado

Garcia-Gaines, R. and S. Frankenstein, 2015. USCS and the USDA Soil Classification system. US Army Corps of Engineers, ERDC/CRREL Tr-15-4, March 2015. https://apps.dtic.mil/dtic/tr/fulltext/u2/a614144.pdf

4.3. TIER 3 GATEWAY TO COMPLEX TOOLS: HOW MUCH LNAPL IS PRESENT?

4.3.1. Comparison of Concawe Tool vs. API LDRM Model

While the Concawe Toolbox includes the Tier 2 LNAPL Volume and Extent Model (de Blanc and Farhat, 2018) for evaluating how much LNAPL is present, another option is to apply the API LDRM Tool. These two tools can be found here:

- *Multi-site LNAPL Tool:* Built into Concawe Toolbox Tier 2 under the questions "How much LNAPL is present?" and "Will LNAPL recovery be effective?"
- *API LDRM Tool:* Download from the API web site here (https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/ldrm); requires Windows operating system. Note there are two separate manuals: Volume 1 provides background theory and conceptual models. Volume 2 is the actual User Guide with help on parameter selection.

4.3.2. Similarities Between Multi-site Tool and LDRM

- Both calculate specific volume, recoverable volume, and transmissivity at individual well locations using the same relationships.
- Both use the f-factor method to calculate residual LNAPL saturation.

4.3.3. Differences Between Multi-site Tool and LDRM

- LDRM has more choices for relative permeability calculation.
- LDRM allows users to account for smear zones above and below the LNAPL lens, while the Multi-site tool does not.
- LDRM allows users to specify a fixed or variable residual saturation or f-factor, while the Multi-site tool uses only a variable f-factor for residual saturation.
- LDRM simulates LNAPL recovery for several kinds of systems, while the Multi-site tool does not simulate LNAPL recovery.
- LDRM is limited to a 3-layer system, while the Multi-site tool considers up to 10 layers.
- LDRM is limited to a single location, while the Multi-site tool calculates LNAPL properties at unlimited locations simultaneously.
- The Multi-site tool estimates spatial variation of transmissivity and LNAPL volumes, while the LDRM does not.

- The Multi-site tool accesses a customizable soil properties database for different soil types, while the LDRM requires users to enter this information manually for every well.

4.3.4. Overview of LDRM

"*The API LNAPL Distribution and Recovery Model (LDRM) simulates the performance of proven hydraulic technologies for recovering free-product petroleum liquid releases to groundwater. Model scenarios included in the LDRM are hydrocarbon liquid recovery using single- and dual-pump well systems, skimmer wells, vacuum-enhanced well systems, and trenches. The LDRM provides information about LNAPL distribution in porous media and allows the user to estimate LNAPL recovery rates, volumes and times.*"

"The Guide has been designed to meet the needs of very busy professionals. As such, the primers and tools can be utilized within 15 to 25 minutes so that information can be gained rapidly. A list of references is also provided to enable more detailed understanding." (API web page).

In general, the LDRM is a very powerful tool to simulate multiphase flow behaviour that controls LNAPL recovery. To run LDRM, it is helpful to have an understanding of capillary pressure relationships (e.g., van Genuchten relationship; van Genuchten, 1980), LNAPL residual saturation concepts such as the f-factor, and the design of LNAPL recovery systems.

4.3.5. Learning More About LDRM: Other Teaching Resources

The Tier 3 Gateway also includes the following LDRM information:

- A short video describing LDRM: https://www.youtube.com/watch?v=dAZi8a58M-U

- A checklist showing the LDRM input screens

- An example of some LDRM output

- A general LDRM flowchart

- LDRM References

- Link to key LDRM documents: https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/ldrm

5. HOW FAR WILL THE LNAPL MIGRATE?

There are three levels of information that are delivered with the Concawe LNAPL Toolbox:

- Tier 1: Simple, Quick Graphics, Tables, Background Information
- Tier 2: Middle Level Quantitative Methods, Tools
- Tier 3: Gateway to Complex Models

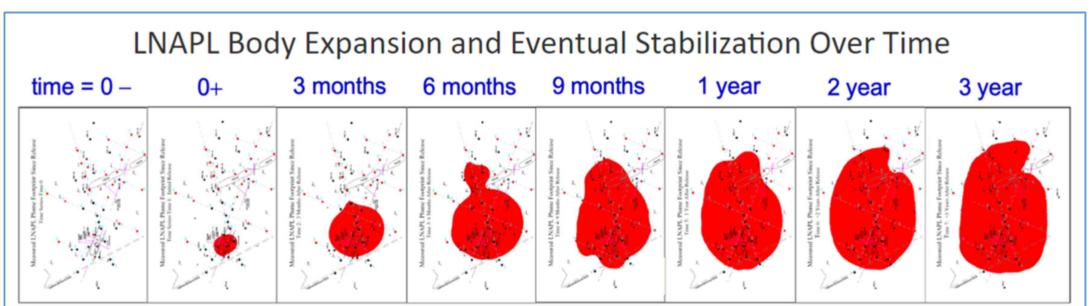
Each of the three Tiers are described below in this Section.

5.1. TIER 1 QUICK INFO: HOW FAR WILL THE LNAPL MIGRATE?

5.1.1. Introduction to LNAPL Body Expansion

The potential for LNAPL expansion is an important consideration when managing the risk from LNAPL at LNAPL sites. Some key conventions/concepts are:

- LNAPL experts typically call the LNAPL mass an "LNAPL Body" to prevent any confusion with a dissolved hydrocarbon plume that may be generated by the LNAPL. The phrase "LNAPL plume" should be avoided.
- LNAPL bodies need energy (pressure) to force the LNAPL at the leading edge of the LNAPL body into the pore space of the unimpacted soils.
- The required pressure can be significant, and once the release of LNAPL to the surface is stopped, the LNAPL body will stabilize at some point on its own accord.
- Recent advances in Natural Source Zone Depletion (NSZD) shows that NSZD is also an important process for limiting LNAPL migration and for stabilizing and even shrinking LNAPL bodies.
- The Tier 1 Quick Info tab shows this graphic of LNAPL body expansion and eventual stabilization over a three-year period:



ITRC LNAPL Training Part 2: LNAPL Characterization and Recoverability – Improved Analysis, 2016.

The figure above shows an example LNAPL body that was released at time 0 and then shows the size of the LNAPL footprint as indicated by monitoring wells over the next three years. The key point is that the footprint of most

LNAPL bodies will stabilize after a few years after the release stops. Sale et al. (2018) describe this important point this way:

"A primary concern at LNAPL sites has been the potential for lateral expansion or translation of LNAPL bodies. Fortunately, long-term monitoring suggests that the extent of LNAPL bodies at older LNAPL releases tend to be stable, even when potentially mobile LNAPL exist within the LNAPL bodies (Mahler et al. 2012b). An important exception to stable LNAPL bodies is new releases. Historically, the primary explanation for the stability of older LNAPL releases has been low LNAPL saturation (fractions of pore space containing LNAPL) and correspondingly low formations conductivities to LNAPL. More recently, Mahler et al. (2012a) added the argument that natural loses of LNAPL play a critical role in controlling lateral expansion or translation of LNAPL bodies. In general, the threshold condition for expanding LNAPL bodies, at older release sites, is LNAPL release rates that are greater than natural source zone depletion rates. Much like dissolved phase petroleum hydrocarbon plumes, the extent of LNAPL bodies can be strongly limited by natural processes."

5.1.2. References

LNAPL, 2014. "LNAPL Training Part 2: LNAPL Characterization and Recoverability – Improved Analysis".

Mahler, N., Sale, T., Lyverse, M., 2012a. A mass balance approach to resolving LNAPL stability. Ground Water 50, 861-871.

Mahler, N., T. Sale, T. Smith, and M. Lyverse, 2012b. Use of Single-Well Tracer Dilution Tests to Evaluate LNAPL Flux at Seven Field Sites, Journal of Ground Water, Vol. 50, No. 6, pp 851-860.

Sale, T., Hopkins, H., Kirkman, A., 2018. Managing Risk at LNAPL Sites. American Petroleum Institute, Washington, DC.

5.2. TIER 2 MODELS/TOOLS: HOW FAR WILL THE LNAPL MIGRATE?

5.2.1. The Kirkman LNAPL Body Additional Migration Tool

5.2.1.1. What the Model Does

This tool, called the Kirkman LNAPL Body Additional Migration Tool, calculates the additional distance that the leading edge of an existing LNAPL plume is expected to migrate until it eventually stabilizes in the presence of Natural Source Zone Depletion (NSZD). To run the model, you need to enter three things about your LNAPL body into the model: 1) a representative LNAPL transmissivity from bail down tests or from transmissivities calculated using the Tier 2 LNAPL Volume and Extent Model; 2) the measured LNAPL body gradient (the slope of the LNAPL body surface); and 3) the current LNAPL body radius (the model makes a simplifying assumption that the LNAPL body is circular).

5.2.1.2. How the Model Works

The model is based on multiple runs of the Hydrocarbon Spill Screening Model (HSSM; Weaver et al., 1994). For each run, an average LNAPL transmissivity (Tn) and gradient (i) were calculated across the oil lens at different times and soil types. These average properties were used as starting conditions to calculate the expected additional growth of an LNAPL plume under an assumed zero-order NSZD rate of 2.0 x 10^{-6} m/day using the steady-state relationship for a circular source derived by Mahler (Mahler et al., 2012).

The plot shows the calculated LNAPL plume length increase for different average values of LNAPL transmissivity × gradient and piecewise linear fit to the data in the nomograph.

To use the model, the user enters an LNAPL gradient and transmissivity (in metres squared per day), and the estimated additional LNAPL plume growth is calculated from one of the following two equations:

For $Tn \times i \leq 4.0 \times 10^{-4}$,

$$R\ (m) = 262{,}397 \times Tn \times i - 20.1$$

For $Tn \times i > 4.0 \times 10^{-4}$,

$$R\ (m) = 66{,}329 \times Tn \times i + 61.7$$

where R is the length increase of the LNAPL plume in metres.

5.2.1.3. Key Assumptions

The model assumes that there is an unlimited source of LNAPL and that the LNAPL flux is constant. This is an experimental model. Incorporation of HSSM (Weaver et al., 1994) and Mahler et al. (2012) represents a non-hysteric methodology where entrapment of LNAPL is ignored and loss rate inputs can account for partitioning and biodegradation losses.

Entrapment of LNAPL has been evaluated (Sookhak Lari et al., 2016; Pasha et al., 2014; Guarnaccia et al., 1997) and demonstrated to slow the rate of LNAPL migration. Current methods to incorporate entrapment require numerical models which are not within the scope of this tool. The lack of incorporating entrapment results in a conservative approach where the upper bound of LNAPL migration extent is estimated. The results of this tool are intended to be used for demonstrating LNAPL body stability by comparing the maximum potential for LNAPL migration to current extent.

The model is useful for estimating the upper bound of LNAPL migration. However, if the calculated LNAPL extent is used in cumulative LNAPL loss and time to depletion estimates then the resulting estimates would overestimate losses and underestimate time to depletion (Sookhak Lari et al., 2016). It is appropriate to use current delineated LNAPL body extent for cumulative loss calculations or time to depletion estimates.

5.2.1.4. Input Data

LNAPL Transmissivity: LNAPL transmissivity can be determined in two general ways:

1. *Computer Models:* Use a multiphase LNAPL model to calculate transmissivity based on soil type, LNAPL properties, and other factors. The Tier 2 LNAPL Volume and Extent Model can be used to easily estimate LNAPL transmissivity, as can LDRM. Sale (2001)

provide methods for determining inputs to environmental petroleum hydrocarbon and recovery models.

2. *Field Measurements (ITRC, 2018):* Conduct field data and analyse the data to calculate the LNAPL transmissivity. ITRC (2018) and ASTM (2013) prescribe three approaches:

    1. *LNAPL Baildown Testing*: Note a computer spreadsheet is available to process the data from baildown tests to determine transmissivity (Charbeneau et al., 2012) (no metric units, however).

    2. *Manual LNAPL Skimming Testing.*

    3. *LNAPL Recovery System Evaluation.*

The ITRC's LNAPL guidance has a detailed discussion of how to measure and use LNAPL transmissivity (ITRC, 2017) as does the ASTM's Standard Guide for Estimation of LNAPL Transmissivity. Units: metres squared per day.

LNAPL Gradient: The change in vertical LNAPL elevation between two points in the area of the LNAPL observation divided by the distance between these points. Units: metre per metre.

Current LNAPL Body Radius: Use maps of mobile LNAPL (a map of the LNAPL that is observed in monitoring wells) to estimate a representative radius of the LNAPL body. If the LNAPL body is not circular, taking the average of each width divided by two in all four directions can be used to obtain the current LNAPL body radius. Units: metres.

5.2.1.5. Developer

This LNAPL tool, sometimes referred to as the Kirkman LNAPL Body Additional Migration Tool, was developed by **Andrew Kirkman** of BP. Reference this way:

Kirkman, A., 2021. LNAPL Body Additional Migration Tool. Andrew Kirkman, BP. Programmed by GSI Environmental for the Concawe LNAPL Toolbox.

5.2.1.6. References

ASTM. 2013. Standard Guide for Estimation of LNAPL Transmissivity. ASTM International.

Charbeneau, R. Kirkman, A., Muthu, R., (2012) API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis.

Guarnaccia, J. , Pinder, G. , Fishman, M. , 1997. NAPL: Simulator Documentation, US EPA.

ITRC, 2018. LNAPL-3: LNAPL Site Management – LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council.

Mahler et al., 2012. A mass balance approach to resolving LNAPL stability, N. Mahler, T. Sale, and M. Lyverse, Ground Water 50(6): 861-571, November/December 2012.

Pasha, A.Y. , Hu, L. , Meegoda, J.N. , 2014. Numerical simulation of a light nonaqueous phase liquid (LNAPL) movement in variably saturated soils with capillary hysteresis, Can. Geotech. J. 51, 1046–1062.

Sale, T. (2001). Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models, American Petroleum Institute Publication No. 4711.

Sookhak Lari, K. , Davis, G.B. , Johnston, C.D. , 2016 Incorporating hysteresis in a multi-phase multi-component NAPL modelling framework; a multi-component LNAPL gasoline example, Advances in Water Resources. 96, 190-201.

Weaver et al., 1994. The Hydrocarbon Spill Screening Model (HSSM); Volume 1: User's Guide, J.W. Weaver, R.J. Charbeneau, B.K. Lien, and J.B. Provost, U.S. EPA, EPA/600/R-94/039a.

5.2.2. Mahler Model

5.2.2.1. What the Model Does

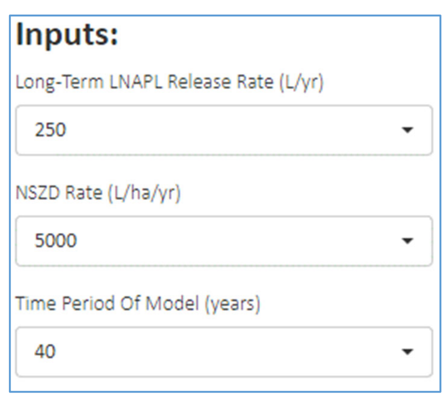
Methods developed by Mahler et al. (2012) illustrate that natural losses of LNAPL (e.g., NSZD) can play an important role in governing the overall extent of LNAPL bodies. This module calculates the overall length of a contiguous LNAPL body, given an inflow of LNAPL rate, NSZD rate, and time period.

5.2.2.2. How the Model Works

The user is able to select a Long-Term LNAPL Release Rate, NSZD Rate, and a Time Period of Model. The output is an estimate for the ultimate LNAPL body length.

5.2.2.3. Key Assumptions

A limitation of the current methodology is the assumption of constant inflow of LNAPL throughout the entire lifetime of the LNAPL Body into the subsurface. Given either the reduction or termination of an LNAPL body, the times for stabilization and LNAPL body length could be much shorter. Additionally, LNAPL migration is not a function of the slope of the water table. Finally, the tool is limited to three different selections for the Long-term LNAPL Release Rate, three different selections for NSZD Rate, and three different selections for Time Period.



5.2.2.4. Input Data

The input data consist of three types of data:

Long-Term LNAPL Release Rate: The Mahler model assumes a constant, continuing LNAPL release rate to the subsurface. The LNAPL body size eventually will stabilize due the attenuation effects of NSZD. Units: litres per year

NSZD Rate: An estimated or measured NSZD rate for the site. Units: litres of LNAPL biodegraded per hectare per year.

Time Period of Model: The year to see the result. Units: numerical years.

Output Results: The model returns the Estimated Ultimate LNAPL Body Length in units of metres. This is the length that the LNAPL body stabilizes at where the continual entry of LNAPL into the subsurface is balanced by the NSZD rate over the area of the LNAPL body. Units: metres from the LNAPL entry point.

5.2.2.5. Developer

This LNAPL tool was derived from the work of Mahler et al., 2012 by **Poonam Kulkarni**, GSI Environmental. Reference this tool this way:

Kulkarni, P., 2021. LNAPL Migration Calculator based on Mahler et al. Model. Concawe LNAPL Toolbox.

5.2.2.6. References

Mahler, N., Sale, T., Lyverse, M., 2012. A Mass Balance Approach to Resolving LNAPL Stability. Groundwater 50, 861-871.

5.3. TIER 3 GATEWAY TO COMPLEX TOOLS: HOW FAR WILL THE LNAPL MIGRATE?

5.3.1. Overview

The Concawe Toolbox includes a new Tool developed by Andrew Kirkman based on LNAPL mass limitations included in the HSSM conceptual model integrated with LNAPL transmissivity relationships and LNAPL removal via Natural Source Zone Depletion (NSZD) using the Mahler et al. (2012) model (see Section 4.2). This Tier 3 section provides additional information about HSSM and UTCHEM, two tools that can be used to answer the question "How far will the LNAPL migrate?" The 2012 paper by Mahler et al. (2012) presents important findings on how NSZD limits LNAPL migration. Finally, an emerging LNAPL modelling method being developed by GSI's Dr. Sorab Panday is a promising new approach where LNAPL modelling can be performed using a commonly used groundwater model like MODFLOW.

5.3.2. Overview of HSSM

- "HSSM" is an acronym for Hydrocarbon Spill Screening Model.
- Uses analytical relationships to simulate LNAPL movement.
- Simulates vertical LNAPL flow through the unsaturated zone.
- Simulates formation and decay of an LNAPL lens at the water table.
- Assumes a circular lens that is not affected by a water table slope.
- Simulates dissolution of LNAPL constituents and dissolved plume migration.

- Older model that requires workarounds to run on 64-bit operating systems like Windows 10.

- NSZD cannot be simulated, so that LNAPL spreading predictions in HSSM will overestimate actual spreading.

- Can be downloaded here: https://www.epa.gov/water-research/hydrocarbon-spill-screening-model-hssm-windows-version.

5.3.3. Overview of UTCHEM

- University of Texas chemical flood simulator developed for the oil industry.

- 3-D finite-difference numerical simulator for NAPL.

- Simulates multiphase, multicomponent, variable temperature systems and complex phase behaviour.

- Accounts for chemical and physical transformations and heterogeneous porous media.

- Uses advanced concepts in high-order numerical accuracy and dispersion control and vector and parallel processing.

- Extremely powerful model but expensive and can be difficult to run.

- Due to its complexity, it is typically only used for more complicated LNAPL/environmental problems.

- Can be run either as a stand-alone program or accessed through GMS package (e.g., https://www.aquaveo.com/software/gms-groundwater-modeling-system-introduction)

5.3.4. Learning More About HSSM and LDRM: Other Teaching Resources

The Tier 3 Gateway also includes the following information:

- A short video describing HSSM and UTCHEM: https://www.youtube.com/watch?v=h6im2Z63DiY

- Overview of Mahler et al. (2012) LNAPL Stability Paper

- Checklist of Input Data for HSSM

- General Flowchart for Running HSSM

- Example Output from HSSM

- UTCHEM Key Processes that Require Input Data

- Example UTCHEM Flowchart for a Surfactant Problem

- An Emerging LNAPL Model: The Panday LNAPL Simulator Based on MODFLOW

5.3.5. References

Aquaveo, 2021. GMS Tutorials UTCHEM. Downloaded Feb. 2021.

Charbeneau, R., Weaver, J., Lien, B., 1995. The Hydrocarbon Spill Screening Model (HSSM). Volume 2: Theoretical Background and Source Codes. U.S. Environmental Protection Agency.

EST, Aqui-Ver, 2006. API Interactive LNAPL Guide. American Petroleum Institute.

Mahler et al., 2012. A mass balance approach to resolving LNAPL stability, N. Mahler, T. Sale, and M. Lyverse, Ground Water 50(6): 861-571, November/December 2012.

Panday, S., P. de Blanc, and R. Falta, in review. Simulation of LNAPL flow in the vadose zone using a single-phase flow equation. Submitted to Groundwater, in review (Feb. 2021).

University of Texas, 2000a. Volume I: User's Guide for UTCHEM-9.0.

University of Texas, 2000b. Volume II: Technical Documentation for UTCHEM-9.0.

Weaver, J.W., R. Charbeneau, J.D. Tauxe, B.K. Lien, and J.B. Provost, 1994. The Hydrocarbon Spill Screening Model (HSSM) Volume 1: User's Guide EPA/600/R-94/039a

6. HOW LONG WILL THE LNAPL PERSIST?

There are three levels of information that are delivered with the Concawe LNAPL Toolbox:

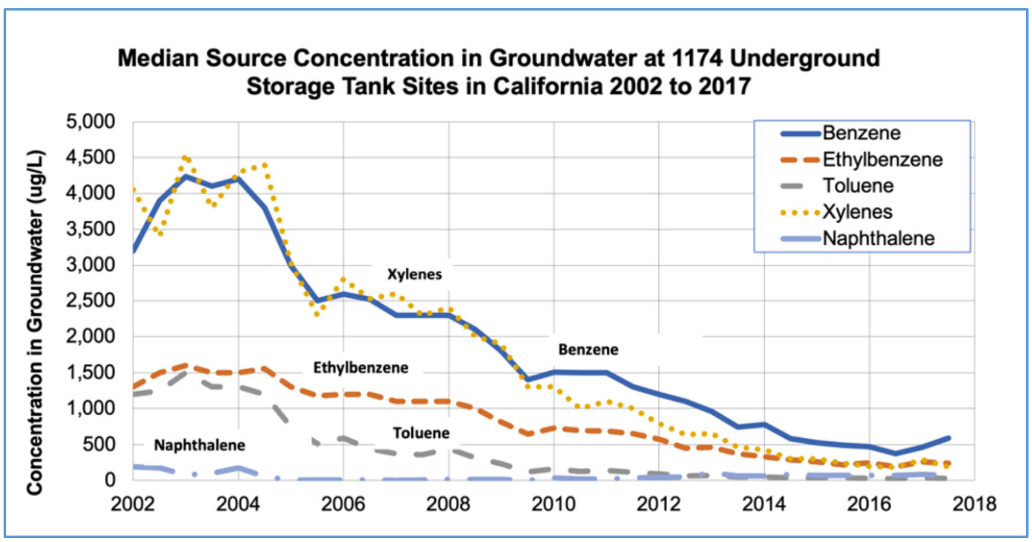
- Tier 1: Simple, Quick Graphics, Tables, Background Information
- Tier 2: Middle Level Quantitative Methods, Tools
- Tier 3: Gateway to Complex Models

Each of the three Tiers are described below in this Section.

6.1. TIER 1 QUICK INFO: HOW LONG WILL THE LNAPL PERSIST?

6.1.1. Introduction

The figure below shows the median concentration in 1,174 Underground Storage Tank Sites in California over time. Because of stricter environmental regulations, the number and magnitude of releases has greatly diminished over time. In addition, almost all of these sites have had some form of source remediation, and all have been subjected to natural attenuation processes. Between 2004 and 2017, the median benzene concentration in groundwater at the highest concentration well in each of the 1,174 sites has been reduced by about 90%, from about 4,000 µg/L to about 500 µg/L (McHugh et al., 2013, 2019).



The table below shows the median change in benzene concentrations and in LNAPL apparent thickness from several hundred Underground Storage Tank Sites in California. Sites where companies were actively recovering LNAPL showed a benzene half-life (the time required for source zone monitoring well concentrations to decrease by 50%) of about 8 years, while sites with LNAPL in monitoring wells but no active remediation exhibited a benzene half-life of about 4 years. During the monitoring period, the thickness of the LNAPL in monitoring wells decreased by about 90% both for sites where active LNAPL recovery was on-going and sites where there was no active LNAPL recovery (Kulkarni et al., 2015).

	Number of Sites	Minimum Monitoring Time Period (years)	Median Apparent LNAPL Thickness in Monitoring Wells During Monitoring Period (meters)	Median Reduction in Apparent LNAPL Thickness in Monitoring Wells Over Monitoring Period (% reduction)	Time for Benzene Groundwater Conc. To Be Reduced by 50% (Half Life) (years)
Sites Where LNAPL is Present and Being Recovered	327	5	1.5	0.87	7.7
Sites Where LNAPL is Present but Not Being Recovered	444	5	0.5	0.91	3.6

6.1.2. References

Kulkarni, P.R., McHugh, T.E., Newell, C.J., Garg, S., 2015. Evaluation of Source-Zone Attenuation at LUFT Sites with Mobile LNAPL. Soil and Sediment Contamination: An International Journal 24, 917-929.

McHugh, T.E., Kulkarni, P.R., Newell, C.J., Connor, J.A., Garg, S., 2013. Progress in Remediation of Groundwater at Petroleum Sites in California. Groundwater 52, 898-907. (Updated by GSI Environmental, 2019).

6.2. TIER 2 MODELS/TOOLS: HOW LONG WILL THE LNAPL PERSIST?

A simple LNAPL lifetime calculator was developed based on a "box model" and mass balance concepts for the Concawe LNAPL Toolbox.

6.2.1. What the Model Does

This simple LNAPL lifetime calculator shows two different models of how Natural Source Zone Depletion (NSZD) will remove LNAPL over time.

- The left graph shows a "zero order" NSZD model where the current NSZD rate stays constant over a long period of time, as suggested by Garg et al. (2017) (see excerpt below; source: Garg et al., 2017).

- The right graph shows a "first order" NSZD model where the current NSZD rate drops in proportion to the mass of LNAPL remaining. Many natural attenuation models assume this type of relationship (e.g., BIOSCREEN model, Newell et al., 1996).

> 3. *Does the NSZD rate change over time? How does LNAPL composition change over long time periods as NSZD progresses?*
>
> While there is considerable temporal variability in measured NSZD rates possibly due to factors such as "signal shredding," soil moisture, etc., there are several lines of evidence that suggest that over decades, the NSZD rate is generally zero order: (1) the presence of controls such as acetate, predation, and so on that may provide a feedback mechanism on the long-term NSZD rate; (2) long-term laboratory studies (e.g., Siddique et al. 2008) showing zero-order behavior at higher hydrocarbon concentrations); (3) the semi-sequenced biodegradation of different buckets observed at Bemidji, add up to a fairly constant bulk
>
> NSZD rate (Ng et al. 2015) (Figure 9); and (4) the hydrocarbon composition literature that shows the potential for sequenced biodegradation of different hydrocarbon chemical classes. Therefore, current knowledge suggests that a zero-order depletion rate can be assumed for much of the life of the LNAPL until a low saturation of LNAPL or a relatively recalcitrant fraction is left, but research is needed to determine if this fraction should be considered important for site management, for example, its magnitude and any persisting secondary water quality effects.

6.2.2. How the Model Works

Given an initial LNAPL body volume and NSZD rate (either via an NSZD study in the field or a using typical NSZD rates in the scientific literature), the model calculates an estimated range when most/all of the LNAPL will be removed by NSZD.

6.2.3. Key Assumptions

The model assumes the user has an estimate of the LNAPL volume remaining in the subsurface (in volume units of total litres of LNAPL in the source zone) and has an estimate for the NSZD rates. Current knowledge suggests that a zero-order depletion rate can be assumed for much of the life of the LNAPL until a low saturation of LNAPL or a relatively recalcitrant fraction is left, but research is needed to determine if this fraction should be considered important for site management, for example, its magnitude and any persisting secondary water quality effects.

Overall, the linear model will present a best-case estimate for the LNAPL lifetime, and the first order model will be more conservative (i.e., may overestimate the LNAPL lifetime).

6.2.4. Input Data

Initial Volume of LNAPL Body: This is the current volume of the LNAPL body in the LNAPL source zone of interest. Users typically use this tool in the area of the LNAPL body where mobile LNAPL is observed (i.e., LNAPL is observed in monitoring wells). This can be difficult to estimate, but typically two methods are used:

1. Use an LNAPL model where the user enters the amount of LNAPL present in monitoring wells, soil data, and stratigraphic information to estimate the LNAPL volume. The Tier 2 calculator in the LNAPL Volume section is designed to provide this information.

2. Use soil sampling data where the LNAPL body is discretized in some way and Total Petroleum Hydrocarbon (TPH) sampling data represent each discretized volume. The concentration of each soil sample is multiplied by the discretized volume and then adjusted using the density of the soil and the density of the LNAPL to convert the final answer to litres of LNAPL in each discretized volume. The LNAPL volume in each separate volume are added together to obtain the total volume of LNAPL. Units: litres of LNAPL in the LNAPL body.

Area of the LNAPL Body: Use maps of the LNAPL body to estimate the area of the LNAPL body. Users typically focus on the area of the mobile LNAPL body where LNAPL is observed in monitoring wells. Units: hectares.

NSZD Rate: Enter the NSZD rate. Typically used measurements methods rely on carbon efflux or temperature generation. See the NSZD Estimations tab, ITRC (2017), or the EnviroWiki for more detailed information about NSZD. NSZD values reported in the literature range from **2,800 to 72,000 litres per hectare per year** with the middle 50% of NSZD values falling between **6,600 to 26,000 litres per hectare per year** (Garg et al., 2017).

Similarly, a recent dataset of 31 distinct sites encompassing over 3,000 measurements from three different methods (DCC-LICOR, Carbon Traps, and Thermal Monitoring) was compiled. Measured average source area NSZD rates ranged from **655 to 152,470 litres per hectare per year**, with a median of **8,750 litres per hectare per year** (Rosansky et. al., 2021). Units: litres of LNAPL biodegraded per hectare per year.

Model Year Start Year: Enter the year for which you have the estimate for the initial volume of the LNAPL body. This could be the initial year of the release or spill if the spill volume was known, or the year that the sampling data were collected and then used to estimate the volume of the LNAPL body. Units: calendar year.

Model End Year: Enter the year you would like to see the results. Users can change this value to see when mass of the LNAPL diminishes to an important endpoint due to NSZD. Units: calendar year.

6.2.5. Developer

This LNAPL tool was developed by **Poonam Kulkarni** of GSI Environmental, Houston, Texas, USA. Reference this way:

Kulkarni, P., 2021. LNAPL Body Lifetime Calculator. Programmed by GSI Environmental for the Concawe LNAPL Toolbox

6.2.6. References

Garg, S., C. Newell, P. Kulkarni, D. King, M. Irianni Renno, and T. Sale, 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Groundwater Monitoring and Remediation 37. (open access; https://ngwa.onlinelibrary.wiley.com/doi/full/10.1111/gwmr.12219).

Newell, C.J., D.T. Adamson, 2005. Planning-Level Source Decay Models to Evaluate Impact of Source Depletion on Remediation Timeframe. Remediation 15.

Newell, C.J., Gonzales, J., McLeod, R. , 1996. BIOSCREEN Natural Attenuation Decision Support System. U.S. Environmental Protection Agency. (https://www.gsi-net.com/en/software/free-software/bioscreen.html)

Palaia, T., J. Fitzgibbons, and P. Kulkarni. 2019. Natural Source Zone Depletion (NSZD). ESTCP Enviro Wiki. Accessed Feb. 2021.

6.3. TIER 3 GATEWAY TO COMPLEX TOOLS: HOW LONG WILL THE LNAPL PERSIST?

6.3.1. Overview

A simple box model is provided in Tier 2 and provides a range of time required for the LNAPL to be removed by Natural Source Zone Depletion (NSZD). Users enter the estimated mass/volume of LNAPL present and the estimated NSZD rate.

Two more sophisticated computer tools that can be used to estimate how long the LNAPL might persist at a site are REMFuel (Falta et al., 2012) and LNAST (Huntley and Beckett, 2002). A short summary of each model is provided below.

6.3.2. USEPA'S REMFuel Model

- REMFuel is a coupled analytical source zone/plume response model distributed by USEPA.
- Based on popular REMChlor model used at chlorinated solvent sites.
- The source zone model includes a box model where the mass of the dissolution product to be modelled is entered and a relationship "gamma" that describes the mass flux out of the source at any time compared to the remaining mass is specified by the user.
- Solute transport model simulates advection, dispersion, retardation, sorption assuming simple 1-D groundwater flow.
- The user can specify any percent of source removal at any time to model plume response to active remediation.
- The user can model plume remediation at any time in three separate spatial zones by increasing first order decay constants.
- NSZD can also be simulated by entering a value for "Source Decay" although there is no discussion in User's Guide on how to do this.
- Key output of the model are graphs showing the concentration (or mass discharge) of the constituents in the dissolved plume vs. distance from source.
- Download model from USEPA web page here: https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=241847.

6.3.3. Overview of API's LNAPL Dissolution and Transport Screening Tool (LNAST)

- LNAST is suite of calculation tools, information about LNAPL, and LNAPL parameter databases. LNAST focuses on LNAPL distribution and fate at the water table. The calculation tool part of LNAST:
- Predicts LNAPL distribution, dissolution, and volatilization over time.
- Calculates downgradient dissolved-phase concentration through time.
- Shows results both with and without hydraulic recovery of LNAPL.
- LNAST simulates the smear zone and the downgradient dissolved plume.

- Combines multi-phase transport, dissolution, and solute transport.
- Accounts for relative permeability effects caused by LNAPL.
- Zones of high LNAPL saturation have much less groundwater flow through them, extending the longevity of these zones.
- Good tool for estimating how long an LNAPL-generated plume will persist.
- Powerful tool to see if LNAPL recovery reduces the longevity of the source and plume.
- Key output is concentration of dissolved constituents in the plume vs. time at an observation well.
- Does not account for NSZD.
- Assumes that remediation occurs shortly after the LNAPL release. You cannot release LNAPL many years ago and then start the remediation now a few decades later.
- LNAST can be downloaded here: https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/evaluating-hydrocarbon-removal.

6.3.4. Learning More About REMFuel and LNAST: Other Teaching Resources

The Tier 3 Gateway also includes the following information:

- A short video describing REMFuel: https://www.youtube.com/watch?v=H8JP8gvZcr8
- A short video describing LNAST: https://www.youtube.com/watch?v=3RNJWFoRLwM
- Checklist of Input Data for REMFuel
- Example Output from REMFuel
- Checklist of LNAST Input Data for LNAST
- Example of LNAST Output Data

6.3.5. References

Falta, R.W., Ahsanuzzaman, A.N.M., Stacy, M., Earle, R.C., 2012. REMFuel: Remediation Evaluation Model for Fuel Hydrocarbons User's Manual. USEPA.

Huntley, D., Beckett, G., 2002. Evaluating Hydrocarbon Removal from Source Zones and Its Effect on Dissolved Plume Longevity and Magnitude. American Petroleum Institute.

7. HOW WILL LNAPL RISK CHANGE OVER TIME?

There are three levels of information that are delivered with the Concawe LNAPL Toolbox:

- Tier 1: Simple, Quick Graphics, Tables, Background Information
- Tier 2: Middle Level Quantitative Methods, Tools
- Tier 3: Gateway to Complex Models

Each of the three Tiers are described below in this Section.

7.1. TIER 1 QUICK INFO: HOW WILL LNAPL RISK CHANGE OVER TIME?

7.1.1. Introduction

The table on the next page shows an approximate way to conceptualize the change in risk as LNAPLs weather. At most LNAPL sites, most of the risk in groundwater due to potential ingestion is due to the amount of benzene that is present in the LNAPL. The higher the mole fraction of benzene in the LNAPL, the higher the potential concentration of dissolved benzene in groundwater. In this example, the composition of a fresh gasoline and a weathered gasoline were taken from a 1990 paper by Johnson et al. (this table is shown to the bottom of the Tier 1 screen). As can be seen in the table, the fresh gasoline had a benzene mole fraction of 0.0093 (calculated from a mass fraction of 0.0076 or about 1% by weight) (column 2). The weathering process removes benzene, and the weathered gasoline mole fraction was 0.0028 (mass fraction of 0.0021) (column 3). When the mole fractions are multiplied by a pure-phase solubility (column 4), a theoretical concentration in groundwater can be calculated for water in perfect equilibrium with the LNAPL (columns 5 and 6). Then, using common regulatory criteria in the U.S. for allowable concentrations in drinking water (column 7), a relative risk (RR) factor was calculated for both the fresh and weathered gasoline (columns 8 and 9) where the equilibrium water concentration is divided by the regulatory criteria. As shown in columns 8 and 9, benzene by far has the highest regulatory risk.

The bottom right of the table shows the cumulative regulatory risk for the BTEX compounds and naphthalene was 3,285 for the fresh gasoline but only 1,020 for the weathered gasoline. Therefore, in this simple example, the risk associated with the LNAPL was reduced by almost 70% when going from a fresh gasoline to the weathered gasoline sample. This is only an example of how the hypothetical risk of LNAPL can change over time due to LNAPL attenuation processes over time. Although each site will be different, in general LNAPL attenuation processes will reduce the risk associated with groundwater ingestion and indoor air exposure pathways over time.

7.1.2. Developer

Charles Newell and Tom McHugh of GSI environmental developed this conceptualization of changing LNAPL risk over time. Reference this way:

Newell, C.J. and T. McHugh, 2021. LNAPL Risk Change Over Time Example, Concawe LNAPL Toolbox.

Change in Risk Due to LNAPL Weathering: A Hypothetical Example

Col. 1	*Col. 2*	*Col. 3*	*Col. 4*	*Col. 5*	*Col. 6*	*Col. 7*	*Col. 8*	*Col. 9*
LNAPL Constituent	Gasoline Mole Fraction	Weathered Gasoline Mole Fraction	Pure-Phase Solubility (mg/L)	Fresh Gasoline Concentration in Water (mg/L)	Weathered Gasoline Concentration in Water (mg/L)	Risk Criteria (mg/L)	Fresh Gasoline Relative Risk (RR) (-)	Weathered Gasoline Relative Risk (RR) (-)
Benzene	0.0093	0.0028	1,750	16	5	0.005	3,248	986
Toluene	0.057	0.041	515	29	21	1	29	21
p-xylene	0.086	0.015	198	17	2.9	10	1.7	0.3
m-xylene	0	0.037	158	0	5.9	10	0	0.6
o-xylene	0	0.027	175	0	4.7	10	0	0.5
Naphthalene	0.003	0.006	32.9	0.11	0.2	0.017	6.5	12
						Total:	**3,285**	**1,020**
							Percent Reduction in Risk Due to Weathering:	**69%**

7.1.3. References

Johnson, P.C., M.W. Kemblowski, and J.D. Colthart. 1990. Quantitative Analysis of Cleanup of Hydrocarbon-Contaminated Soils by In-Situ Soil Venting. Ground Water, Vol. 28, No. 3. May – June 1990, pp 413-429.

7.2. TIER 2 MODELS/TOOLS: HOW WILL LNAPL RISK CHANGE OVER TIME?

An LNAPL Dissolution Calculator has been programmed into the Concawe LNAPL Toolbox.

7.2.1. What the Model Does

This model calculates the theoretical concentrations of LNAPL constituents downgradient of an LNAPL release over time caused by dissolution processes alone.

7.2.2. How the Model Works

A known volume of LNAPL is released to the subsurface. The LNAPL is comprised of several components whose volume fractions and densities are known. The unidentified fraction of the LNAPL is a mixed petroleum product with unknown components, but with a known average molecular weight and density.

The LNAPL establishes a lens in the groundwater with a known width and average thickness. Groundwater flows through the LNAPL lens and dissolves the LNAPL constituents, reducing the remaining volume of LNAPL and changing its composition as the more soluble compounds dissolve out of the LNAPL. Equilibrium between the water and LNAPL within the lens is assumed, so that the concentration of constituents downgradient of the LNAPL are equal to the effective solubility of the LNAPL constituents. Effective solubility is the solubility of a pure phase component times its mole fraction in the LNAPL.

The key strengths of the model are:

- The model is simple and easy to understand.
- Because of its simplicity, the model can be modified by users if needed.

Weakness of the model are:

- Equilibrium is unlikely to be completely achieved at actual sites, so the model over-estimates downgradient aqueous phase concentrations.
- The explicit solution scheme can become inaccurate or unstable if the time step is too large.

7.2.3. Key Assumptions

Key assumptions of the model are as follows:

- Volume is conserved upon fluid mixing.

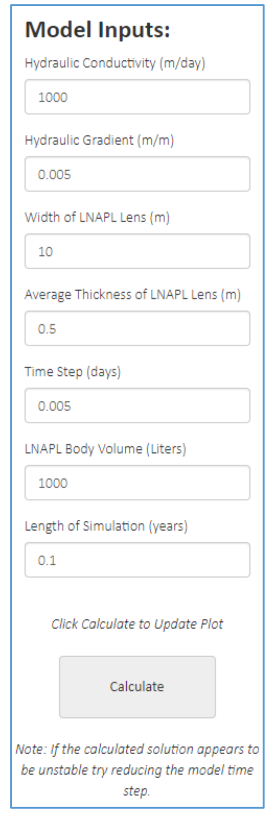
- The concentration of a constituent in the aqueous phase in equilibrium with the LNAPL is the constituent's mole fraction in the LNAPL times the constituent's pure phase solubility.

- Water exiting the LNAPL lens is saturated with each LNAPL constituent; i.e., there is perfect mixing between groundwater and LNAPL constituents in the LNAPL lens.

- LNAPL does not impede groundwater flow.

- Fluid densities and solubilities do not change significantly with temperature.

- The change in total number of moles in the LNAPL is slow over the time period of the model.



7.2.4. Input Data

Hydraulic Conductivity: Enter the water saturated hydraulic conductivity of the aquifer with the LNAPL from pump tests, slug tests, or from estimates based on soil properties of the geologic media. Typical values (Newell et al., 1996):

- Silts: 1×10^{-6} - 1×10^{-3} cm/s (8.6×10^{-4} to 0.86 metres per day)

- Silty sands: 1×10^{-5} - 1×10^{-1} cm/s (8.6×10^{-3} to 86 metres per day)

- Clean sands: 1×10^{-3} - 1 cm/s (8.6×10^{-1} to 864 metres per day)

- Gravels: > 1 cm/s (> 864 metres per day)

For simple estimates, just enter the hydraulic conductivity of the aquifer soils. Sophisticated users can adjust this value to account for relatively permeability effects caused by the LNAPL. Units: metres per day.

Hydraulic Gradient: From Newell et al. (1996): The slope of the groundwater potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table. Typical values range from 0.0001 - 0.05 metres per metre. Units: metre per metre.

Width of LNAPL Lens: Based on maps of the LNAPL body, enter the width across the LNAPL lens (normal to the groundwater flow direction). Units: metres.

Average Thickness of LNAPL Lens: The typical thickness of the LNAPL body. Typical values range from 0.1 to 2 metres. This value can be determined from soil boring logs where LNAPL presence is determined from closely spaced soil samples, from visual observations, field instruments such as PIDs, LNAPL dye tests, or from models. Units: metres.

Time Step: Enter a value ranging from 0.1 to 10 days. Sometimes a trial-and-error approach must be used to obtain results from the dissolution model. If the calculated solution appears to be unstable, try reducing the model time step. Units: days.

LNAPL Body Volume: This is the current volume of the LNAPL body in the LNAPL source zone of interest. Users typically use this tool in the area of the LNAPL body where mobile LNAPL is observed (i.e., LNAPL is observed in monitoring wells). This can be difficult to estimate, but typically two methods are used:

1. Use an LNAPL model where the user enters the amount of LNAPL present in monitoring wells, soil data, and stratigraphic information to estimate the LNAPL volume. The Tier 2 calculator in the LNAPL Volume section is designed to provide this information.

2. Use soil sampling data were the LNAPL body is discretized in some way and Total Petroleum Hydrocarbon (TPH) sampling data represent each discretized volume. The concentration of each soil sample is multiplied by the discretized volume and then adjusted using the density of the soil and the density of the LNAPL to convert the final answer to metres cubed of LNAPL in each discretized volume. The LNAPL volume in each separate volume are added together to obtain the total volume of LNAPL. Units: liters of LNAPL in the LNAPL body.

Length of Simulation: Enter the year at which the groundwater concentration is desired. Year zero is the corresponds to the LNAPL body volume entered. Typical values: 1 to 100 years. Units: integer (not calendar year).

LNAPL Constituent Properties: Enter the name, volume fraction, molecular weight, solubility, and density of each LNAPL constituent.

LNAPL Constituents Chemistry Inputs:

	LNAPL Constituents	Volume fraction	Molecular weight (g/mol)	Solubility (mg/L)	Density (g/cm³)
1	benzene	0.89	78.1	1770	0.87
2	toluene	0.1	92.1	530	0.74
3	other	0.01	100	10	0.78
4					
5					

Showing 1 to 5 of 5 entries

Volume Fraction of LNAPL Constituents: Enter the volume fraction of each LNAPL constituent. See the Composition (Mass Fractions) of Fresh and Weathered Gasolines from Tier 1 for typical values (note mass fractions and volume fractions will vary slightly). For fresh gasoline typical values for benzene are 0.5 to 1.0, although this value has changed significantly over time. These values must equal 1. Units: cubic metres of constituent per cubic metre of LNAPL.

Molecular Weight of LNAPL Constituents: Enter the molecular weight of each known LNAPL constituent. For the unknown or "other" fraction, if the LNAPL is gasoline, the molecular weight of decane (142 g/mol) is often used. Otherwise, a similar molecular weight can be assumed. Units: grams per mole.

Solubility of LNAPL Constituents: Enter the solubility of each LNAPL constituent. For the unknown or "other" fraction, a value less than 10 mg/L can be used to represent these compounds. Units: milligrams per litre.

Density of LNAPL Constituents: Enter the density of each known LNAPL constituent. For the "other" fraction, use the values provided in the table to the right (from page 10 of Source Report A of the LA LNAPL Recoverability Study: https://www.gsi-net.com/en/publications/la-lnapl-recoverability-study.html); or use values from the literature; or perform laboratory tests to measure your LNAPL properties. The API document Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models" is a useful compilation of testing methods.

	Density @ 15°C (g/cm^3)
Gasoline	0.729
Diesel	0.827
JP A/B	0.77 – 0.79
Crude Oil	0.832 – 0.914

https://www.api.org/oil-and-natural-gas/environment/clean-water/groundwater/lnapl/~/media/97D9B7561D34477F85D790DC1E3CCDBB.ashx

Units: grams per cubic centimetre.

7.2.5. Developer

This LNAPL tool was developed by **Dr. Phillip de Blanc**, GSI Environmental, Houston, Texas, USA based on Mayer and Hassanizadeh (2005). Reference this way:

de Blanc, P., 2021. LNAPL Dissolution Calculator. Programmed by GSI Environmental for the Concawe LNAPL Toolbox.

7.2.6. References

Mayer and Hassanizadeh, 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids – Principles and Observations, Alex Mayer and S. Majid Hassanizadeh, Ed., Water Resources Monograph 17, American Geophysical Union, USA.

7.3. TIER 3 GATEWAY TO COMPLEX TOOLS: HOW WILL LNAPL RISK CHANGE OVER TIME?

7.3.1. Overview

The risk posed by the toxic components of an LNAPL plume is a function of the constituents' concentration in groundwater in contact with the LNAPL. A multi-component LNAPL dissolution model based on the LNAPL constituent mole fraction and Raoult's law (Mayer and Hassanizadeh, 2005) is provided in Tier 2 and shows how the dissolved constituent concentrations immediately downgradient of an LNAPL body change over time.

A more sophisticated computer tool, API's LNAST model, also shows the change in dissolved phase LNAPL concentrations over time (Huntley and Beckett, 2002). It is summarized below. Finally, two other key LNAPL attenuation studies, a LNAPL mass balance developed by Ng et al. (2014)

and a 2003 report about weathering of jet fuel LNAPL, are also reviewed below.

7.3.2. Overview of API's LNAPL Dissolution and Transport Screening Tool (LNAST)

- LNAST is suite of calculation tools, information about LNAPL, and LNAPL parameter databases. LNAST focuses on LNAPL distribution and fate at the water table. The calculation tool part of LNAST:
- Predicts LNAPL distribution, dissolution, and volatilization over time.
- Calculates downgradient dissolved-phase concentration through time.
- Shows results both with and without hydraulic recovery of LNAPL.
- Simulates the smear zone and the downgradient dissolved plume.
- Combines multi-phase transport, dissolution, and solute transport.
- Accounts for relative permeability effects caused by LNAPL.
- Zones of high LNAPL saturation have much less groundwater flow through them, extending the longevity of these zones.
- Good tool for estimating how long an LNAPL-generated plume will persist.
- Powerful tool to see if LNAPL recovery reduces the longevity of the source and plume.
- Key output is concentration of dissolved constituents in the plume vs. time at an observation well.
- Does not account for Natural Source Zone Depletion (NSZD).
- Assumes that remediation occurs shortly after the LNAPL release. You cannot release LNAPL many years ago and then start the remediation now a few decades later. The REMFuel model will do this, see Tier 3 of "How long will LNAPL persist?" portion of the Concawe LNAPL Toolbox.
- LNAST can be downloaded here: https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/evaluating-hydrocarbon-removal.

7.3.3. Learning More About LNAST: Other Teaching Resources

The Tier 3 Gateway also includes the following information:

- A short video describing LNAST: https://www.youtube.com/watch?v=3RNJWFoRLwM

- Checklist of Input Data for LNAST
- Example Output from LNAST
- Description of Ng et al. (2014) LNAPL Model Example of LNAST Output Data
- Summary of Parsons Fuel LNAPL Weathering Study

7.3.4. References

Garg, S., Newell, C., Kulkarni, P., King, D., Adamson, D., Irianni Renno, M., Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Ground Water Monitoring and Remediation, Vol 37.

Huntley, D., Beckett, G., 2002. Evaluating Hydrocarbon Removal from Source Zones and Its Effect on Dissolved Plume Longevity and Magnitude. American Petroleum Institute.

Mayer and Hassanizadeh., 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids, Alex S. Mayer and S. Majid Hassanizadeh, Ed., AGU Water Resources Monograph 17, 2005.

Ng, G.-H.C., Bekins, B.A., Cozzarelli, I.M., Baedecker, M.J., Bennett, P.C., Amos, R.T., 2014. A mass balance approach to investigating geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN. Journal of Contaminant Hydrology 164, 1-15.

Ng, G.-H.C., B.A. Bekins, I.M. Cozzarelli, M.J. Baedecker, P.C. Bennett, R.T. Amos, and W.N. Herkelrath. 2015. Reactive transport modelling of geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN. Water Resources Research 51: 4156–4183.

Parsons, 2003. Final Light Non-Aqueous Liquid Weathering at Various Fuel Release Sites, 2003 Update. Air Force Center for Environmental Excellence.

8. WILL LNAPL RECOVERY BE EFFECTIVE?

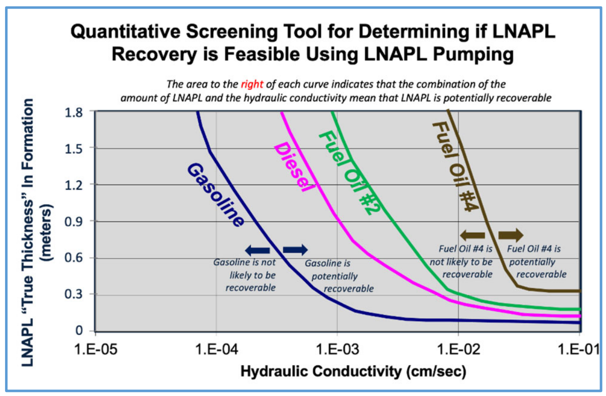
There are three levels of information that are delivered with the Concawe LNAPL Toolbox:

- Tier 1: Simple, Quick Graphics, Tables, Background Information
- Tier 2: Middle Level Quantitative Methods, Tools
- Tier 3: Gateway to Complex Models

Each of the three Tiers are described below in this Section.

8.1. TIER 1 QUICK INFO: WILL LNAPL RECOVERY BE EFFECTIVE?

8.1.1. Introduction



The Texas Risk Reduction Program developed guidance for managing LNAPL in the subsurface and provided a quantitative screening tool for knowing when LNAPL is potentially recoverable using total fluids submersible pumps. This tool was developed by entering certain site conditions into the numerical multiphase transport model ARMOS. Key assumptions included: petroleum hydrocarbon contamination and a single submersible total-fluids recovery pump with an inlet set at depth of 3 feet below static water level. The figure to the right summarizes the results of numerous model simulations configured for different fuel viscosities, hydraulic conductivities, product thicknesses, and recovery system drawdown that are combined with assumptions of what constitutes recovery effectiveness at this site.

This LNAPL recoverability screening tool is used this way:

1. Select the applicable LNAPL product curve and
2. Plot the point that approximates the "true LNAPL thickness" and the hydraulic conductivity of the unit in which the LNAPL is found. If the plotted point is on the right side of the product curve, LNAPL is recoverable using the total fluids system configuration described above.

Note the "true LNAPL thickness" is not commonly used now but was meant to estimate the thickness of the LNAPL in the formation with very high LNAPL saturations. It can be estimated by taking the specific volume of LNAPL (see the Tier 1 tab for the first question in this Concawe Toolbox "How much LNAPL is present?" and then dividing by the porosity of the soil containing the LNAPL). Alternatively, an older, less accurate method is to use the chart provided below from 1990 U.S. EPA LNAPL guidance where one can convert the apparent LNAPL thickness in a monitoring well to a "true LNAPL thickness."

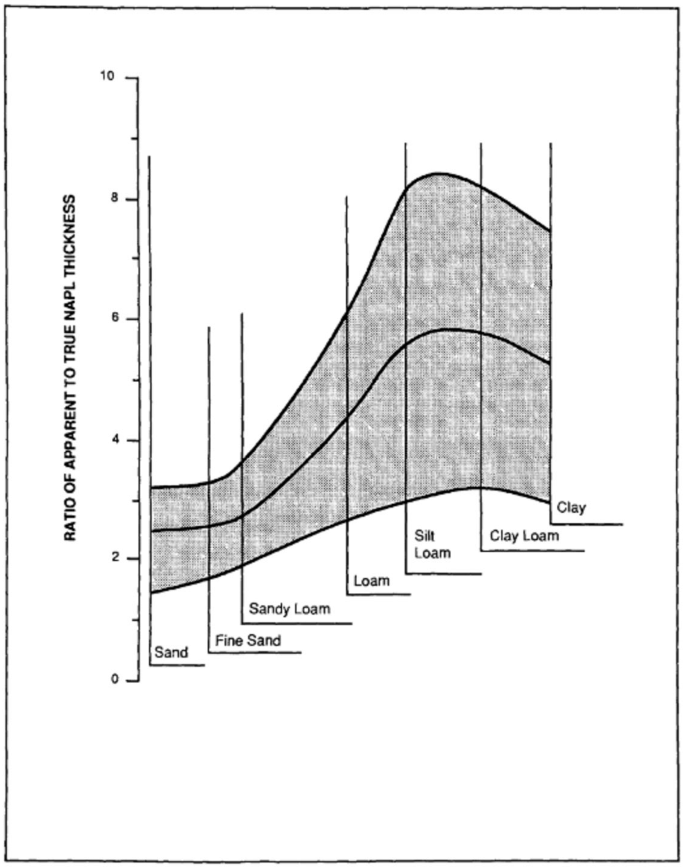


Figure 7. Ratio of Apparent to True NAPL Thickness for Various Soil Types

8.1.2. References

Reidy, P.J., Lyman, W.J., Noon, D.C., 1990. Assessing UST Corrective Action Technologies. Early Screening of Clean-up Technologies for the Saturated Zone. U.S. EPA, EPA/600/2-90/027.

Texas Risk Reduction Program, 2008. Risk-Based NAPL Management, TRRP-32. Austin, Texas.

8.2. TIER 2 MODELS/TOOLS: WILL LNAPL RECOVERY BE EFFECTIVE?

LNAPL transmissivity is now an accepted way to determine if LNAPL is likely to be recoverable using conventional technologies such as LNAPL skimming or pumping. Based on guidance from ITRC (2018), the key threshold for LNAPL recovery is the LNAPL transmissivity has to be higher than this general range of numbers: 0.0093 to 0.074 m2/day. The range should be interpreted as a grey area for recoverability. If the calculated or measured LNAPL transmissivity is below that the lowest value, then there is a high probability that LNAPL hydraulic recovery will not to be cost effective or efficient. If above the highest number, then hydraulic recovery has a much higher likelihood of being feasible.

There are three approaches to obtain LNAPL transmissivity values:

1. Taking field measurements;
2. Using the Tier 2 LNAPL Volume and Extent Model programmed in the LNAPL Toolbox;
3. Using the Tier 2 LNAPL Transmissivity Calculator programmed in the LNAPL Toolbox.

8.2.1. Measuring LNAPL Transmissivity

LNAPL transmissivity concepts are described in ITRC (2018) and ASTM (2013) and prescribe three commonly used approaches:

1. LNAPL Baildown Testing. Note a computer spreadsheet is available to process the data from baildown tests to determine transmissivity (Charbeneau et al., 2012) (no metric units, however).
2. Manual LNAPL Skimming Testing.
3. LNAPL Recovery System Evaluation.

The resulting transmissivity can be compared against the **0.0093 to 0.074 m^2/day** transmissivity threshold described above to determine if LNAPL can be recovered effectively.

8.2.2. Use the LNAPL Volume and Extent Model to Obtain LNAPL Transmissivity

Go to Section 4.2 to understand what this tool does, what input data are required, and how to get transmissivity data as an output. The resulting transmissivity can be compared against the **0.0093 to 0.074 m^2/day** transmissivity threshold described above to determine if LNAPL can be recovered effectively.

8.2.3. Use the LNAPL Transmissivity Calculator

8.2.3.1. What the Model Does

This tool calculates the following variables that indicate LNAPL volume and mobility at a single location for a single soil type: LNAPL specific volume, transmissivity, and Darcy flux. LNAPL transmissivity is the product of the average LNAPL hydraulic conductivity times the thickness of the LNAPL lens. Large transmissivity values indicate that LNAPL has greater potential to move through the subsurface than small values and suggests that LNAPL may be more easily mobilized or recovered. Transmissivity is often used as an indication of when LNAPL recovery is no longer practical.

8.2.3.2. How the Model Works

The tool is based on the methodology of the API's LDRM (Charbeneau, 2007). The user enters parameters for the soil type, fluid properties, and the thickness of LNAPL observed in a monitoring well. LNAPL saturations are computed over the LNAPL thickness to calculate specific volume. Transmissivity is then calculated by integrating the saturation-dependent relative permeability over the LNAPL thickness. The product of the average relative permeability and the saturated hydraulic conductivity for the LNAPL is the LNAPL transmissivity. The transmissivity divided by the LNAPL thickness, then multiplied by the LNAPL gradient is the LNAPL Darcy flux (volume of LNAPL per unit area of formation). The model uses an “f-factor” approach in which the LNAPL residual saturation is a function of the LNAPL thickness across the lens (Charbeneau, 2007).

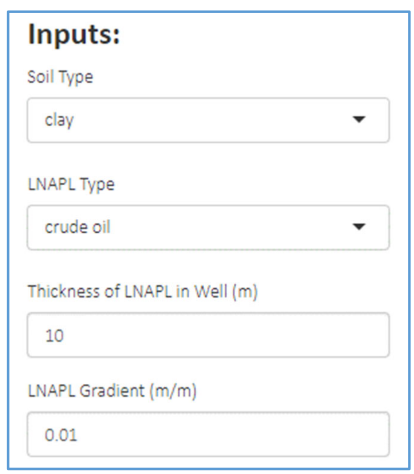
Based on guidance from ITRC (2018), the key transmissivity threshold for LNAPL recovery is a value above: **0.0093 to 0.074 m^2/day.** The range should be interpreted as a grey area for recoverability. If the calculated or measured LNAPL transmissivity is below that the lowest value, then there is a high probability that LNAPL hydraulic recovery will not to be cost effective or efficient. If above the highest number, then hydraulic recovery has a much higher likelihood of being feasible.

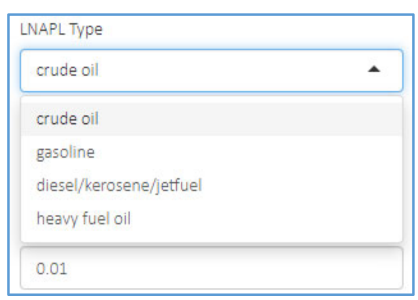
8.2.3.3. Key Assumptions

The model assumes that the LNAPL is in hydrostatic equilibrium with the surrounding media. Relative permeability is calculated by combining the Mualum model with the van Genuchten soil characteristic curve parameters (Charbeneau, 2007).

The model uses default values for various soil and LNAPL properties. Soil properties can be found in Carsel and Parrish (1988), and LNAPL properties can be found in Mercer and Cohen (1990) and Charbeneau (2003).

8.2.3.4. Input Data





Users enter these data:

Soil Type: Select the soil type that best describes the geologic media that contains the LNAPL.

LNAPL Type: Select either crude oil, gasoline, diesel/kerosene/jet fuel, or heavy fuel oil.

Thickness of LNAPL in Well: Enter the thickness of the LNAPL accumulation in the well. Units: metres.

LNAPL Gradient: The change in vertical LNAPL elevation between two points in the area of the LNAPL observation divided by the distance between these points. Units: metre per metre.

8.2.3.5. Output from Model

The key output from the model is LNAPL transmissivity in units of metres squared per day, and supplemental values shown to the right.

Transmissivity from Calculator	
Parameters	*Values*
LNAPL Transmissivity (m^2/d)	**0.0016**
Key threshold for LNAPL recoverability: LNAPL Transmissivity above this range (numbers *within* this range are in a grey zone for recoverability)	0.0093 to 0.074 m^2/day

Additional Results from Calculator	
Parameters	*Values*
Maximum LNAPL Height (m)	11
Height of LNAPL/ Air Interface above Water (m)	10
Relative density (unitless)	0.84
van Genuchten M (unitless)	0.083
LNAPL Specific Volume (m^3/m^2)	0.22
LNAPL Mobile Specific Volume (m^3/m^2)	0.15
LNAPL Average Relative Permeability (unitless)	0.17
LNAPL Average Hydraulic Conductivity (m/d)	0.00014
LNAPL Darcy Flux (m/d)	1.6E-05
Average LNAPL Volumetric Content (unitless)	0.05
LNAPL Average Seepage Velocity (m/d)	0.00032

8.2.3.6. Developer

This LNAPL tool was developed by **Dr. Phillip de Blanc**, GSI Environmental, Houston, Texas, USA. Reference this way:

de Blanc, P., 2021. LNAPL Transmissivity Calculator, Concawe LNAPL Toolbox.

8.2.3.7. References

ASTM. 2013. Standard Guide for Estimation of LNAPL Transmissivity. ASTM International.

Charbeneau, R. Kirkman, A., Muthu, R., (2012) API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis.

ITRC, 2018. LNAPL-3: LNAPL Site Management - LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council.

Charbeneau, 2007. LNAPL Distribution and Recovery Model (LDRM) Volume 1: Distribution and Recovery of Petroleum Hydrocarbon Liquids in Porous Media, Randall J. Charbeneau, American Petroleum Institute.

8.3. TIER 3 GATEWAY TO COMPLEX TOOLS: WILL LNAPL RECOVERY BE EFFECTIVE?

8.3.1. LNAPL Conceptual Site Model (LCSM)

"The LCSM is the collection of information that incorporates key attributes of the LNAPL body with site setting and hydrogeology to support site assessment and corrective action decision-making. The LCSM integrates information and considerations specific to the LNAPL body relating to the risks of the contaminant source, exposure pathways, and receptors. The content of the LCSM will typically evolve over time as different phases of the corrective action process require different information. What remains consistent is the emphasis in the LCSM on characterizing and understanding the source component, the LNAPL." (ITRC, 2018). At sites where LNAPL recovery is key remediation question, the LSCM can be refined and improved by using computer models and/or LNAPL transmissivity to better understand the potential for LNAPL recovery.

8.3.2. Computer Models

Several computer models are available to help understand if LNAPL can be recovered effectively:

1. The API's LDRM model can be used to determine how much LNAPL can be recovered. For an overview of LDRM, see Tier 3 of "How much LNAPL is present?"

2. The USEPA's REMFuel model allows users to develop a simple box model of BTEX and oxygenates in an LNAPL source zone, simulate a historical release, and see the effects of removing some fraction of LNAPL in the current timeframe or sometime in the future. For an overview of REMFuel, see Tier 3 of "How long will LNAPL persist?"

3. The UTCHEM model can simulate LNAPL recovery and is particularly useful for extremely complex LNAPL problems and for modelling surfactant remediation projects. For an overview of UTCHEM, see Tier 3 of "How far will LNAPL migrate?"

4. The API LNAST model can be used to see the impact of LNAPL recovery on dissolved plumes. For an overview of LNAST, see Tier 3 of "How will LNAPL risk change over time?"

8.3.3. LNAPL Transmissivity

More recently there has a been a move to use LNAPL transmissivity as a key metric to evaluate LNAPL recoverability (e.g., ITRC, 2017). The ITRC's "Top Three Things To Know about LNAPL Transmissivity" is reproduced to the right.

Top Three Things to Know about LNAPL Transmissivity (T_n)

1. T_n describes a basic relationship between LNAPL drawdown in a well and LNAPL flow to that well. This makes it a representative metric for LNAPL recoverability by any hydraulic method—including skimming, pumping, vacuum extraction, or manual bailing.
2. T_n measurements must be used in context of the overall LCSM; identifying potentially confined or perched conditions and understanding seasonal changes are important to accurately measuring and appropriately using T_n as a metric.
3. T_n measurements are relevant to LNAPL saturation remedial objectives (e.g., recovering NAPL to the maximum extent practicable, or controlling LNAPL migration) and are not directly relevant to composition-based remedial objectives (e.g., meeting dissolved-phase groundwater standards).

The use of transmissivity has been catalysed by a general consensus that hydraulic recovery of LNAPL (skimmer wells, trenches, groundwater pumping, etc.) has a **Technology Threshold Metric** consisting of LNAPL transmissivity greater than 0.1 to 0.8 ft2/day (0.0093 to 0.074 m2/day). This metric may be used as a decision point for remedial system operation or technology transitions (ITRC, 2018). For example, in the State of Michigan, LNAPL guidance states "*if the NAPL has a transmissivity greater than 0.5 ft2/day, it is likely that the NAPL can be recovered in a cost-effective and efficient manner unless a demonstration is made to show otherwise.*" (ITRC, 2018). ITRC also describes five sites in detail that were used as the basis of this range (Section 2.3).

LNAPL transmissivity can be determined in two general ways:

1. *Computer Models:* Using a multiphase LNAPL model to calculate transmissivity based on soil type, LNAPL properties, and other factors. The Tier 2 LNAPL Subsurface Volume and Extent Model can be used to easily estimate LNAPL transmissivity, as can LDRM. Sale (2001) provide methods for determining inputs to environmental petroleum hydrocarbon and recovery models.

2. *Field Measurements (ITRC, 2018, Section 2.0):* Conduct field data and analyse the data to calculate the LNAPL transmissivity. ITRC (2018) and ASTM (2013) prescribe three approaches:

    1. *LNAPL Baildown Testing:* Note a computer spreadsheet is available to process the data from baildown tests to determine transmissivity (Charbeneau et al., 2012) (no metric units, however).

    2. *Manual LNAPL Skimming Testing.*

    3. *LNAPL Recovery System Evaluation.*

8.3.4. Learning More About Computer Models: Other Teaching Resources

The Tier 3 Gateway also includes the following information:

- A short video describing LDRM: https://www.youtube.com/watch?v=dAZi8a58M-U
- A short video describing REMFuel: https://www.youtube.com/watch?v=H8JP8gvZcr8
- A short video describing UTCHEM: https://www.youtube.com/watch?v=h6im2Z63DiY
- A short video describing LNAST: https://www.youtube.com/watch?v=3RNJWFoRLwM

8.3.5. References

ASTM. 2013. Standard Guide for Estimation of LNAPL Transmissivity. ASTM International.

Charbeneau, R. Kirkman, A., Muthu, R., (2012) API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis.

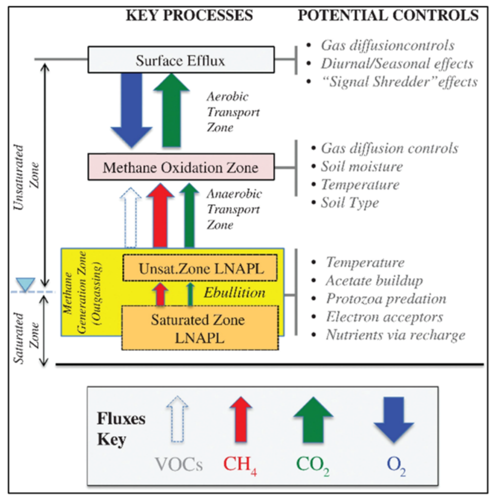
ITRC, 2018. LNAPL-3: LNAPL Site Management - LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council.

Sale, T. (2001). Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models, American Petroleum Institute Publication No. 4711.

9. HOW CAN ONE ESTIMATE NSZD?

9.1. TIER 1 QUICK INFO: HOW CAN ONE ESTIMATE NSZD?

9.1.1. What is Natural Source Zone Depletion (NSZD)?



NSZD describes the loss of LNAPL due to various processes, the most important of which is biodegradation (ITRC, 2009; ITRC, 2018). A series of research projects have determined that this depletion is occurring at much faster rates than first thought, up to 1,000's to 10,000's of litres of LNAPL being biodegraded per hectare per year (Johnson et al., 2006; Sihota et al., 2011; McCoy et al., 2015; Garg et al., 2017). Additionally, Garg et al. (2017) describes an overview of the latest research and key processes controlling NSZD (see figure to right). As such, NSZD is becoming an important factor in the Conceptual Site Model (CSM) and may be incorporated into site management strategies.

NSZD values reported in the literature range from **2,800 to 72,000 litres per hectare per year** with the middle 50% of NSZD values falling **between 6,600 to 26,000 litres per hectare per year** (Garg et al., 2017). Similarly, a dataset of 31 distinct sites encompassing over 3,000 measurements from three different methods (DCC-LICOR, Carbon Traps, and Thermal Monitoring) was compiled. Measured average source area NSZD rates ranged from **655 to 152,470 litres per hectare per year**, with a median of **8,750 litres per hectare per year** (Rosansky et. al., 2021).

9.1.2. Key NSZD Resources

Overview of Natural Source Zone Depletion (NSZD): Processes, Controlling Factors and Composition Change (Garg et al. 2017)

EnviroWiki: Natural Source Zone Depletion (NSZD)

ITRC (2018) Appendix B: Natural Source Zone Depletion (NSZD)

Concawe, 2020. "Detailed Evaluation of Natural Source Zone Depletion at a Paved Former Petrol Station" Concawe Report no. 13/20. https://www.concawe.eu/publication/detailed-evaluation-of-natural-source-zone-depletion-at-a-paved-former-petrol-station/

Garg, S., Newell, C.J., Kulkarni, P.R., King, D.C., Adamson, D.T., Renno, M.I., and Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Groundwater Monitoring & Remediation, 32(3): 62-81. doi: 10.1111/gwmr.12219.

ITRC (Interstate Technology Regulatory Council), 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL . Washington, D.C.: Interstate Technology Regulatory Council, LNAPLs Team.

ITRC, 2018. LNAPL-3: LNAPL Site Management – LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council. March 2018.

Johnson, P., Lundegard, P. and Liu, Z., 2006. Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites—I: Site-Specific Assessment Approach. Groundwater Monitoring & Remediation, 26:82-92. doi:10.1111/j.1745-6592.2006.00114.x.

Lundegard, Paul D., and Paul C. Johnson, 2006. Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites - II: Application to a Former Oil Field. Ground Water Monitoring and Remediation 26 (4): 93-106. https://doi.org/10.1111/j.1745-6592.2006.00115.x.

McCoy, K., Zimbron, J., Sale, T. and Lyverse, M., 2015. Measurement of Natural Losses of LNAPL Using CO2 Traps. Groundwater, 53: 658-667. doi:10.1111/gwat.12240.

Rosansky, S., Moore, S., DeRuzzo, G., McHugh, T., Kulkarni, P., Li, B., 2021. Evaluation and Demonstration of Techniques to Support Natural Source Zone Depletion at Multiple Sites. Draft Technical Report. Prepared for: NAVFAC EXWC.

Sihota, N.J., Singurindy, O., Mayer, K.U., 2011. CO2-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer. Environ. Sci. Technol., 2011, 45 (2), pp 482-488. doi: 10.1021/es1032585.

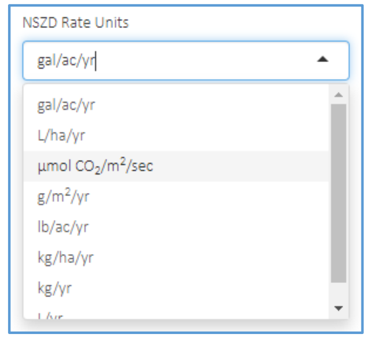
9.2. TIER 2 MODELS/TOOLS: HOW CAN ONE ESTIMATE NSZD?

Two tools are provided in the Tier 2 Natural Source Zone Depletion (NSZD) section of the Concawe LNAPL Toolbox:

- A NSZD Rate Converter
- A NSZD Temperature Enhancement Calculator

9.2.1. NSZD Rate Converter Tool

9.2.1.1. What the Model Does



NSZD rates are reported in a variety of ways as shown by several options in the tool's pulldown menu. Practitioners typically report NSZD in units of volume of LNAPL biodegraded per area per time, such as "gallons per acre per year" in most of the NSZD projects performed in the United States. The NSZD Rate Converter Tool converts typical measures of NSZD rates between metric and imperial, as well as converting from carbon dioxide flux (in units of µmol CO2 per square metre per second) to mass or volume of LNAPL degraded per area per time (ex. litres of LNAPL biodegraded per hectare per year).

9.2.1.2. How the Model Works

The user is able to select an LNAPL type or representative compound, enter an NSZD value and select starting units, and select a final desired unit of mass or volume of LNAPL degradation.

9.2.1.3. Key Assumptions

For converting from a carbon dioxide flux in units of µmol/m2/sec to an LNAPL volume or mass per area per time, the table below summarizes densities and molecular weights applied for each LNAPL type or representative compound. The default parameters apply the density of fresh gasoline (0.77 g/mL), and the molecular weight of octane (114.2 g/mol).

LNAPL Type or Representative Compound	Density (g/mL)	Molecular Weight (g/mol)
Benzene	0.88	78.1
Octane	0.70	114.2
Decane	0.73	142.3
Fresh Gasoline	0.77	95.0
Fresh Diesel	0.83	200.0
Fresh Jet Fuel	0.80	185.0

9.2.1.4. Developer

This LNAPL tool was developed by **Poonam Kulkarni** of GSI Environmental, Houston, Texas, USA. Reference this way:

Kulkarni, P., 2021. NSZD Rate Converter, Concawe LNAPL Toolbox.

9.2.2. NSZD Temperature Enhancement Calculator

9.2.2.1. What the Model Does

Hydrocarbon degradation can be enhanced with increases in temperature (Sustained Thermally Enhanced LNAPL Attenuation [STELA]) (Zeman et al., 2014; Kulkarni et al., 2017). Temperatures in the subsurface can be enhanced by a variety of technologies, such as installing electrical resistance heaters in the LNAPL zone; using clear plastic sheets (i.e., soil solarization) to provide solar heating; using solar swimming pool heaters and closed loop borehole heat exchangers (Kulkarni et al., 2015).This model uses the Arrhenius Law to estimate the potential NSZD rate enhancement with any externally created temperature increase up to 45 °C.

9.2.2.2. How the Model Works

Arrhenius Law estimates for most biological systems, the temperature coefficient is 2.0 (i.e., rates will double with a 10 °C increase in temperature) (Atlas and Bartha 1986; Riser-Roberts 1992).

$Q_{10} = R_2/R_1^{[10/(T2-T1)]}$

Where

Q_{10} = temperature coefficient, typically 2.0

R_1 = NSZD Rate at temperature T_1

R_2 = NSZD Rate at temperature T_2

T_1 = Initial temperature (°C)

T_2 = Final temperature (°C)

9.2.2.3. Key Assumptions

For mesophilic anaerobic digestors, optimum temperature range between 30 and 38 °C (Metcalf and Eddy, 1991; Gerardi, 2003). Maximum temperature approximated to be 40 °C, after which bacterial populations decline.

9.2.2.4. Developer

This LNAPL tool was developed by **Poonam Kulkarni** of GSI Environmental, Houston, Texas, USA. Reference this way:

Kulkarni, P., 2021. NSZD Temperature Enhancement Calculator, Concawe LNAPL Toolbox.

9.2.2.5. References

Atlas, R.M. , and R. Bartha. 1986. Microbial Ecology: Fundamentals and Applications. Menlo Park, California : Benjamin- Cummings.

Gerardi, M.H. 2003. The Microbiology of Anaerobic Digesters. Hoboken, New Jersey : John Wiley & Sons.

Metcalf and Eddy. 1991. Wastewater Engineering—Treatment, Disposal, and Reuse. 3rd ed. New York: McGraw-Hill Publishing Company.

Kulkarni, P.R., Newell, C.J., Sale, T., Irianni Renno M., Stockwell, E., Hopkins, H., Malander, M., Chillemi, J., Higinbotham, J.H. Sustainable Thermally Enhanced LNAPL Attenuation (STELA) Using Soil Solarization. Platform Presentation at the Third International Symposium on Bioremediation and Sustainable Environmental Technologies, May 18-21, 2015. Miami, Florida.

Kulkarni, P.R., King, D.C., McHugh, T.E., Adamson, D.T., Newell, C.J., 2017. Impact of Temperature on Groundwater Source Attenuation Rates at Hydrocarbon Sites. Groundwater Monitoring & Remediation, 37(3): 82-93.

Riser-Roberts, E. 1992. Bioremediation of Petroleum Contaminated Sites. Boca Raton, Florida : CRC Press Inc.

Zeman, N.R. , M.I. Renno , M.R. Olson , L.P. Wilson , T.C. Sale , and S.K. De Long . 2014. Temperature impacts on anaerobic biotransformation of LNAPL and concurrent shifts in microbial community structure. Biodegradation 25: 569–585.

9.3. TIER 3 GATEWAY TO COMPLEX TOOLS: HOW CAN ONE ESTIMATE NSZD?

9.3.1. NSZD Overview

- Natural Source Zone Depletion (NSZD) has emerged as an important new remediation alternative for LNAPL sites. Key references and a description of what they explain about NSZD are provided below:
- The ITRC's (2018) LNAPL Site Management—LCSM Evolution, Decision Process, and Remedial Technologies guidance is heavily influenced by the developments in measuring and applying NSZD for LNAPL site management, with over 100 specific mentions of NSZD in the document and a detailed NSZD appendix. More importantly, it provides detailed information on three frequently used NSZD assessment methods:
    - The gradient method, based on soil gas composition,
    - Carbon dioxide flux-based methods, including Carbon Traps and dynamic closed flux chambers (i.e., DCC-LI-COR), and
    - The biogenic heat monitoring method (Thermal Monitoring).
- Key vendors for these methods are:
    - EnviroFlux (Carbon Traps)
    - LI-COR (DCC- LI-COR)
    - Thermal NSZD (Thermal Monitoring)
- Garg et al.'s (2017) Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change provides a detailed review of how NSZD developed, key NSZD processes,

potentially NSZD-controlling factors, and how NSZD affects the composition of LNAPL (see graphic to right). It is based on roughly 100 technical references.

- Kulkarni et al.'s (2020) Application of Four Measurement Techniques to Understand Natural Source Zone Depletion Processes at an LNAPL Site describes an extensive research project where four different NSZD measurement techniques were used at a site and then compared.

- Lari et al.'s (2019) Natural Source Zone Depletion of LNAPL: A Critical Review Supporting Modelling Approaches discusses key NSZD processes required to model NSZD and the capabilities of 36 models to accommodate 21 important phenomena.

- ESTCP's Environmental Wiki has an entry describing NSZD where the significance of NSZD is discussed along with NSZD stoichiometry, the gaseous expression of NSZD through gas evolution, and measuring temperature to determine NSZD (Palaia, T., J. Fitzgibbons, and P. Kulkarni, 2019).

- CRC CARE's (2018) Technical Report 44: Technical Measurement Guidance for LNAPL Natural Source Zone Depletion provides practical guidance on the measurement of NSZD rates using various available methods. The document applies to hydrocarbon sites that have a need for theoretical, qualitative, or quantitative understanding of NSZD processes. Its Appendix B contains a checklist for practitioners.

9.3.2. Additional NSZD Resources

- Short video developed for the EnviroWiki explaining carbon trap technology: https://www.youtube.com/watch?v=4KF1uRIOZoQ

- Short video developed for the EnviroWiki explaining ThermalNSZD technology: https://www.youtube.com/watch?v=oh3WFyrtUL0

- What NSZD rates are seen at hydrocarbon sites, a table from Garg et al., 2017 and from Rosansky et al., 2021

- What Enhanced NSZD rates are possible with low level heating

9.3.3. References

Atlas, R.M. , and R. Bartha. 1986. Microbial Ecology: Fundamentals and Applications . Menlo Park, California : Benjamin- Cummings.

Garg, S., Newell, C., Kulkarni, P., King, D., Adamson, D., Irianni Renno, M., Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Ground Water Monitoring and Remediation 37.

ITRC. 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. Washington, D.C.: Interstate Technology Regulatory Council, LNAPLs Team.

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Kulkarni, P.R., Newell, C.J., King, D.C., Molofsky, L.J. and Garg, S. 2020. Application of Four Measurement Techniques to Understand Natural Source Zone Depletion Processes at an LNAPL Site. Groundwater Monit R, 40: 75-88.

Lari, S. Kaveh, Greg B Davis, John L Rayner, Trevor P Bastow, and Geoffrey J Puzon. 2019. Natural Source Zone Depletion of LNAPL: A Critical Review Supporting Modelling Approaches. Water Research 157: 630–46. Open Access.

Palaia, T., J. Fitzgibbons, and P. Kulkarni. 2019. Natural Source Zone Depletion (NSZD). ESTCP Enviro Wiki. Accessed Feb. 2021.

Riser-Roberts, E. 1992. Bioremediation of Petroleum Contaminated Sites . Boca Raton, Florida : CRC Press Inc.

Rosansky, S., Moore, S., DeRuzzo, G., McHugh, T., Kulkarni, P., Li, B., 2021. Evaluation and Demonstration of Techniques to Support Natural Source Zone Depletion at Multiple Sites. Draft Technical Report. Prepared for: NAVFAC EXWC.

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10. ADDITIONAL RESOURCES

List of Key Terms and Definitions

Chemical Properties of LNAPLs and Key Constituents

Soil Capillary Pressure Data

10.1. LIST OF KEY TERMS AND DEFINITIONS FROM LA LNAPL WORKGROUP PROJECT

BATT	Best available treatment technology. BATT is a term used here for groundwater cleanup technologies that is similar to the concept of Best Available Technology (BAT). BAT has been employed to select water treatment technologies in California by considering the costs, benefits, and effectiveness of a particular technology. Section 1
BTEX	Benzene, Toluene, Ethyl benzene, Xylene (BTEX). These are four of the most common constituents of LNAPL that dissolve from the LNAPL and can migrate in moving groundwater. Section 2
CPT	Cone penetrometer. The CPT is a specialized geotechnical rig that is used to determine the geology of the subsurface. Section 3.1.3
Dean-Stark analysis	A chemical test to determine how much NAPL fills the pore space of a gravel, sand, or silt sample. In this method, water is first evaporated from the sample, a solvent is then used to extract any oil in the sample. Gravimetric relationships and considerations of bulk and solid density are then used to calculate total LNAPL saturation. Section 3.3.1
FID	Flame ionization detector. This is a device to determine the amount of chemical vapors that are emitted by a soil sample. Section 3.1.2
Formation LNAPL thickness	This is the actual thickness of the subsurface soil that is impacted by LNAPL, sometimes called "*True LNAPL Thickness*". Not all of the subsurface soil is filled with LNAPL. Sections 1.2, 3.3.2, 4.1
Free LNAPL	LNAPL that is hydraulically connected in the pore space and has the potential to be mobile in the environment (ASTM, 2007) Sections 1.2, 4.2.3
LIF	Laser induced fluorescence. This is a method to determine the presence of LNAPL in the subsurface. The illumination source is forced through the subsurface soil on direct-push type drilling rigs. The light causes PAH compounds to fluoresce. Section 3.1.3
LNAPLs	Light non-aqueous phase liquids. These are lighter-than-water separate phase liquids, such as crude oil, gasoline, diesel fuel, etc., that can migrate into the subsurface and form either free, mobile, or residual LNAPL. Section 1.1
LNAPL mobility	The ability of LNAPL to move in the subsurface at the local scale. It is a function of both the LNAPL fluid properties (density and viscosity) and of the intrinsic permeability of the formation. There are different methods to express mobility, including a method that calculates LNAPL "inherent mobility." Section 4.0
LNAPL relative permeability	The ratio of LNAPL permeability to intrinsic permeability of the formation. It is a measure of how mobile an LNAPL accumulation is in the subsurface. Section 4.1
LNAPL Transmissivity	(LNAPL transmissivity is a measure of how much LNAPL can be transmitted horizontally through the subsurface in an existing LNAPL zone.
Macropores	Macropores are relatively large openings in soils that can be caused by plant roots or animals. Macropores control NAPL transport in fine-grained sediments, and lead to small volume NAPL pockets isolated as "islands" within water-saturated media (Johnson and Assali, 2010). The macropores in the vadose zone are typically too small to be defined by current delineation technologies. Section 1.2
Mobile LNAPL	Free LNAPL that is moving laterally or vertically in the environment under prevailing hydraulic conditions. Sections 1.2, 4.0
Mobile Saturation	The LNAPL saturation level above which naturally occurring capillary forces prevent

NAPLs	Non-aqueous phase liquids. Separate phase organic liquids in the subsurface. Section 1.1
NRC	National Research Council. A national research organization funded by the U.S. Federal government that publishes books and reports on a wide range of issues, including groundwater contamination. Section 7.0
NSZD	Natural source zone depletion. The process where natural processes will remove LNAPLs from the subsurface by naturally occurring physical, chemical, and biological processes. Section 4.3
PAH	Polycyclic aromatic hydrocarbons. A class of chemicals that typically have lower solubility and are heavier than the BTEX compounds. Section 3.1
PID	Photo ionization detector. This is a device to determine the amount of chemical vapors that are emitted by a soil sample. Section 3.1.2
Residual LNAPL	LNAPL that is hydraulically discontinuous and immobile under prevailing conditions. Residual LNAPL can be thought of as "individual blobs of LNAPL in individual pores" in a gravel, sand, or silt. This concept is complex, with several different conceptual models on how to apply this value, and five methods to determine a value for residual saturation. Sections 1.2, 3.3, 4.0, 5.0
Residual saturation	The LNAPL saturation level below which naturally occurring capillary forces prevent LNAPL from moving, making the LNAPL immobile. Sections 1.2, 4.0
ROI	Radius of influence. This is a general term for the radius around a treatment well or treatment point that is treated by a particular groundwater cleanup technology. Section 5.3
Specific volume	In a given area, the volume of LNAPL divided by the area. This is a calculated value of the actual amount of LNAPL present in an area divided by the area. This would be the thickness of LNAPL that would remain in an LNAPL zone if the soil and water in that area were hypothetically removed. Section 3.3
Stable body	A LNAPL body that is no longer moving laterally. Section 1.2
Submerged LNAPL	LNAPL that is found well below the water table due to a historical release, followed by a rising water table. Most submerged LNAPL is in the residual form, and conventional floating LNAPL conceptual models do not apply. Submerged LNAPL is found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s. Sections 1.2, 3.3, 4.1
Unconfined LNAPL	LNAPL near the water table of an unconfined formation. Out-of-date conceptual models of LNAPL often referred to this as "floating LNAPL."
Well LNAPL thickness	Observed monitoring well LNAPL thickness. Terms that others have used to describe the observed monitoring well thickness are "apparent thickness" and "observed thickness" Sections 1.2, 3.3.1

Los Angeles LNAPL Workgroup, 2015. Final Report for the LA Basin LNAPL Recoverability Study. . Los Angeles LNAPL Workgroup, Western States Petroleum Association.

10.2. CHEMICAL PROPERTIES OF LNAPLS AND KEY CONSTITUENTS

	Density @ 15°C (g/cm^3)	Viscosity (cp)	Interfacial Tension (dynes per cm)
Gasoline	0.729	0.355 – 0.659	50
Diesel	0.827	Wide range	4 - 28.2
JP A/B	0.77 – 0.79	1.18 -1.59	50 (API 4729)
Crude Oil	0.832 – 0.914	Wide range	25-30.5

Los Angeles LNAPL Workgroup, 2015. Final Report for the LA Basin LNAPL Recoverability Study. . Los Angeles LNAPL Workgroup, Western States Petroleum Association.

Table 1. Representative properties of selected LNAPL chemicals commonly found at Superfund sites (U.S.EPA, 1990), water, and selected petroleum products (Lyman and Noonan, 1990)

Chemical	*Density†* *(g/cm^3)*	*Dynamic† Viscosity (cp)*	*Water† Solubility (mg/l)*	*Vapor† Pressure (mm Hg)*	*Henry's Law† Constant (atm-m^3/mol)*
Methyl Ethyl Ketone	0.805	0.40	2.68 E+05	71.2	2.74 E-05 [(2)]
4-Methyl-2-Pentanone	0.8017	0.5848	1.9 E+04	16	1.55 E-04 [(2)]
Tetrahydrofuran	0.8892	0.55	3 E+05[(1)]	45.6 [(2)]	1.1 E-04 [(2)]
Benzene	0.8765	0.6468	1.78 E+03	76	5.43 E-03 [(1)]
Ethyl Benzene	0.867	0.678	1.52 E+02	7	7.9 E-03 [(1)]
Styrene	0.9060	0.751	3 E+02	5	2.28 E-03
Toluene	0.8669	0.58	5.15 E+02	22	6.61 E-03 [(1)]
m-Xylene	0.8642 [(1)]	0.608	2 E+02	9	6.91 E-03 [(1)]
o-Xylene	0.880 [(1)]	0.802	1.7 E+02	7	4.94 E-03 [(1)]
p-Xylene	0.8610 [(1)]	0.635	1.98 E+02 [(1)]	9	7.01 E-03 [(1)]
Water	0.998 [(6)]	1.14 [(6)]	----	----	----
Common Petroleum Products					
Automotive gasoline	0.72-0.76 [(3)]	0.36-0.49 [(3)]	----	----	----
#2 Fuel Oil	0.87-0.95	1.15-1.97 [(5)]	----	----	----
#6 Fuel Oil	0.87-0.95	14.5-493.5 [(4)]	----	----	----
Jet Fuel (JP-4)	~0.75	~0.83 [(5)]	----	----	----
Mineral Base Crankcase Oil	0.84-0.96 [(6)]	~275[(4)]	----	----	----

† Values are given at 20°C unless noted.
(1) Value is at 25°C.
(2) Value is at unknown temperature but is assumed to be 20°- 30°C.
(3) Value is at 15.6°C.
(4) Value is at 38°C.
(5) Value is at 21°C.
(6) Value is at 15°C.

Newell, C.J., S.D. Acree, R.R. Ross, and S.G. Huling, 1995. Light Nonaqueous Phase Liquids. Ground Water Issue Paper. U.S. Environmental Protection Agency

10.3. SOIL PROPERTIES RESOURCES

Because the critical LNAPL thickness required to overcome the pore entry pressure of the formation is greater than that observed in the well, capillary forces in the formation would prevent the LNAPL from flowing.

Common soil properties and Brooks-Corey and van Genutchen parameters (Carsel and Parrish, 1988):

		Bulk Den.		Brooks & Corey Param.		van Genuchten Param.		
Soil	**Porosity**	**(g/cm^3)**	**K_w (m/d)**	**P_c head (m)**	**λ**	**N**	**α (1/m)**	**m**
Clay	0.38	1.64	0.048	125.	0.09	1.09	0.8	0.0826
Clay loam	0.41	1.56	0.062	0.53	0.31	1.31	1.9	0.237
Loam	0.43	1.51	0.25	0.28	0.56	1.56	3 6	0.359
Loamy sand	0.41	1.56	3.5	0.081	1.28	2.28	12.4	0.561
Silt	0.46	1.43	0.06	0.62	0.37	1.37	1.6	0. 70
Silt loam	0.45	1.46	0.11	0.5	0.41	1.41	2.	0.291
Silty clay	0.36	1.70	0.0048	2	0.09	1.09	0.5	0.0826
Silty clay loam	0.43	1.51	0.017	1	0.23	1.23	1	0.187
Sand	0.43	1.51	7.1	0.069	1.68	2.68	14.5	0.627
Sandy clay	0.38	1.64	0.029	0.37	0.23	1.23	2.7	0.187
Sandy clay loam	0.39	1.62	0.31	0.17	0.48	1.48	5.9	0.324
Sandy loam	0.41	1.56	1.1	0.13	0.89	1.89	7.5	0.471

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Table 17. Consensus of the most probable (MP) and possible (P) USCS classification per USDA texture classification.

	USCS classification						
	SSURGO (2014) *Table 8* WES (1961) *Table 9* Wilson et al. (1965) *Table 10* Rollings and Rollings (1996) *Table 11* Curtis (2005) *Table 12*		Ayers et al. (2011) *Table 13*		Baylot et al. (2013) *Table 14*	FASST (2004) *Table 15*	
USDA Classification	MP	P	MP	P	MP	MP	Consensus
Sand	SM	SP-SM	SW, SP	—	SP	SP	SP
Loamy Sand	SM	CL	SM	SC	SM	SM	SM
Sandy Loam	SM	ML, CL	SM	—	SC	SM	SM
Sandy Clay Loam	CL	SC	SC	—	SC	SC	SC
Sandy Clay	SC, CL	—	SC	CL	SC	SC	SC,
Loam	CL	ML	ML	—	CL	ML	CL
Silt Loam	CL	ML	ML	—	SM	ML	ML
Silt	ML	—	ML	—	ML	ML	ML
Clay Loam	CL	—	CL, MH	—	CL	CL	CL
Silty Clay Loam	CL	ML, CH	MH	—	CL	CL	CL
Clay	CH, CL	GC	CH	CL	CH	CH	CH
Silty Clay	CH, CL	—	CL, MH	—	CL	CH	CH

Garcia-Gaines, R. and S. Frankenstein, 2015. USCS and the USDA Soil Classification system. US Army Corps of Engineers, ERDC/CRREL Tr-15-4, March 2015. https://apps.dtic.mil/dtic/tr/fulltext/u2/a614144.pdf

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