Accepted Manuscript

Quarterly Journal of Engineering Geology and Hydrogeology

A New Toolbox for Managing Sites Impacted by Light Non-Aqueous Phase Liquids (LNAPLs)

Charles J. Newell, Phillip de Blanc, Kenia Whitehead, Brandon Sackmann, Markus Hjort & Eleni Vaiopoulou

DOI: https://doi.org/10.1144/qjegh2024-079

To access the most recent version of this article, please click the DOI URL in the line above. When citing this article please include the above DOI.

Received 16 May 2024
Revised 8 August 2024
Accepted 9 August 2024

A New Toolbox for Managing Sites Impacted by Light Non-Aqueous Phase Liquids (LNAPLs)

Charles J. Newell[1], Phillip de Blanc[a], Kenia Whitehead[b], Brandon Sackmann[b], Markus Hjort[c], Eleni Vaiopoulou[c*]

[a] GSI Environmental Inc., 2211 Norfolk Suite 1000, Houston, Texas, 77098, USA

[b] GSI Environmental, 1115 West Bay Drive NW, Suite 202

Olympia, Washington, 98502, USA

[c] Concawe (Scientific Division of European Fuel Manufacturers Association), Bd du Souverain

165, 1160 Bruxelles, Belgium

* Correspondence: water@concawe.eu

Keywords: LNAPL; volume, migration, risk, longevity, remediation

ABSTRACT

The Concawe LNAPL Toolbox is one of the first completely web-based tools for managing and remediating light non-aqueous phase liquids (LNAPL) impacted sites. An off-line downloadable version is also available for users who do not want to access it via the internet. LNAPLs are typically historic hydrocarbons released into soils and groundwater, such as liquid fuels, crude oil, and condensates. The toolbox was developed by Concawe, the Scientific Division of European Fuel Manufacturers Association, with the support of the engineering and environmental science-consulting agency GSI Environmental. The toolbox, written on the R-Shiny platform, was released in 2022 and includes over 20 different tools, such as, for example, infographics, nomographs, calculators, mobility models, videos, and checklists. These tools are organized into three tiers, with Tier 1 offering basic graphics and essential information, Tier 2 providing simple quantitative models and calculators, and Tier 3 featuring access and explanations of more complex tools. The toolbox is designed to address six key questions that are important for environmental consultants and regulators managing LNAPL sites, including determining the amount of LNAPL, estimating LNAPL migration and persistence, assessing LNAPL risk over time, determining the effectiveness of LNAPL recovery, and estimating Natural Source Zone Depletion (NSZD). The Concawe LNAPL Toolbox is accessible free of charge via a webpage on an internet browser or by downloading the toolbox for use on a personal computer.

1.0 INTRODUCTION

Ever since the foundation of Concawe in 1963, the association has studied the impacts of the refining sector on the environment and ways to mitigate these impacts. Light Non-Aqueous Phase Liquids (LNAPLs) are non-dissolved hydrocarbons (e.g., crude oils, gasoline, and diesel) that exist as a separate, undissolved phase in the subsurface at some sites with legacy releases of fuels (Sale et al., 2018). They are referred to as "light" because most petroleum hydrocarbons are less dense than water (Tomlinson et al. 2017). The behavior of LNAPLs is complex, making it important to understand factors such as the amount of LNAPL present at a site, its potential for migration, the possibility of recovery and remediation, changes in composition over time, persistence, and the rate of natural attenuation (Suthersan et al., 2015). Understanding the behavior of LNAPL in the subsurface is crucial for making appropriate site management decisions, particularly in the context of environmental remediation and risk assessment (ITRC, 2018).

To address this complexity and to help make better remediation decisions, Concawe has developed the Concawe LNAPL Toolbox (Newell et al., 2021; Strasert et al., 2021) with support from GSI Environmental. The toolkit is a comprehensive yet user-friendly web-based tool that provides essential information to the LNAPL remediation community (Figure 1). The toolbox is intended to be a clear, transparent tool that regulators can use to validate site information and make informed decisions using sound science. Further, practitioners can utilize the toolbox to enhance their understanding of their LNAP site and improve their site's Conceptual Site Model (CSM).

2.0 METHODS

The Toolbox was written using the R-Shiny platform (https://shiny.rstudio.com) which gave the developers access to the R statistical programming language, graphing and mapping tools, with some detailed tools written in Python. 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.

3.0 RESULTS: SIX KEY LNAPL QUESTIONS

The tool is structured around six key questions that are often asked at LNAPL sites:

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

Each question is addressed using a three-tier approach. At the highest level, information that can be easily accessed and quickly viewed is presented in Tier 1. Tier 2 offers a variety of quantitative models, tools, and calculators for further analysis. Lastly, Tier 3 serves as a gateway to access more advanced, established models that are available elsewhere. First, users decide which LNAPL management question they would like to address, then determine which Tier they would like to apply as shown in Table 1. Since the Tool was introduced

3.1 CONTENT SUMMARY: HOW MUCH LNAPL IS PRESENT?

The Tier 1 answer to this question first provides a summary of the concept of LNAPL specific volume. This metric represents the volume of LNAPL per unit area of the formation. It can be thought of as the thickness of LNAPL that would remain in an LNAPL zone if the soil and water were removed in a hypothetical scenario. Tier 2 provides a new tool for determining the volume of subsurface LNAPL that has been developed for the Concawe LNAPL Toolbox, an extension of the LNAPL Distribution and Recovery Model (LDRM), which was developed for the American Petroleum Institute (API) by Dr. Randall Charbeneau of the University of Texas (Charbeneau, 2007). This new tool offers several enhancements such as the ability to accommodate multiple soil layers, multiple locations, and a highly accurate integration method with automatic interpolation. The LDRM is widely used to determine the subsurface LNAPL specific volume (D_o) and transmissivity (T_n) at a single location based on user input for up to three soil layers. However, a limitation of the software is that a separate input file is needed to calculate LNAPL D_o and T_n at each location where LNAPL apparent thickness has been measured. This can make the process time-consuming and expensive when many measurements are needed.

To overcome these limitations, the Multi-Site LNAPL Volume and Extent Model was developed for the Toolbox to calculate D_o and T_n. The simultaneous determinations of D_o and T_n at many locations can save a significant amount of time when many locations must be analyzed. A total LNAPL volume is estimated as an area-weighted average of the calculated thicknesses at each well location.

The Tier 3 module for the "How Much LNAPL is Present" question compares the Concawe LNAPL Toolbox the older, , API LDRM Model. Table 2 shows the differences between these two tools.

3.2 Content Summary: How Far Will the LNAPL Migrate?

The Tier 1 module for the answer this question provides a general conceptual model for LNAPL migration in the subsurface (Newell et al., 2021):

- "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 because the pressure becomes insufficient to drive LNAPL into additional pore spaces.
- Recent advances in Natural Source Zone Depletion (NSZD) show that NSZD is also an important process for limiting LNAPL migration and for stabilizing and even shrinking LNAPL bodies."

For the Tier 2 module, two quantitative tools were provided: 1) the Kirkman LNAPL Body Additional LNAPL Migration Tool (Newell et al., 2021); and 2) An LNAPL migration model developed by Mahler et al. (2012). The Kirkman LNAPL Body Additional Migration Tool, developed specifically for the LNAPL Toolbox, is used to estimate the additional distance that the leading edge of an existing LNAPL body is expected to migrate until it stabilizes in the presence of NSZD. To use the model, three inputs are required: 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; and 3) the current LNAPL body radius. The model assumes that the LNAPL body is circular for simplification purposes (Figure 2). The Mahler tool is based on a peer reviewed equation (Mahler et al., 2012) that assumes a constant source of LNAPL release to groundwater that is attenuated by NSZD processes and provides an estimate of the ultimate extent of LNAPL migration based on simplified source scenario.

The Tier 3 module introduces users to two historical LNAPL models, the U.S. Environmental Protection Agency's Hydrocarbon Spill Screening Model (HSSM) (Charbeneau et al., 1995) and University of Texas chemical flood simulator (UTCHEM); U. Texas, 2000). The Tier 3 elements consist of a short video, general flowcharts for running these more complex models, required input data, and example output data.

3.3 Content Summary: How Long Will the LNAPL Persist?

The Tier 1 module for the answer to this question provides a graph of the decrease in median concentration of BTEX (benzene, toluene, ethylbenzene, and xylenes) at underground storage tank sites in California over time (McHugh et al., 2013) updated for the Concawe LNAPL Toolbox. Between the years of 2004 and 2017, a significant reduction in the median concentration of benzene in groundwater was observed at the highest concentration well at each of 1,174 sites. Specifically, the median concentration was reduced by approximately 90%, from an initial level of around 4,000 µg/L to a final level of around 500 µg/L.

The Tier 2 module provides a box model of an LNAPL source zone, where the mass of the LNAPL present in the source zone is used along with the removal rate of LNAPL from NSZD to estimate a range of potential source lifetimes. Two different model expressions are used: 1) a zero-order model where the NSZD rate does not change over time; and 2) a first order model where the NSZD rate drops over time in proportion to the remaining LNAPL mass over time. In the Tier 3 module, the U.S. Environmental Protection Agency's REMFuel model (Falta et al., 2012) and API's LNAST Model (Huntley and Beckett, 2002) are highlighted and explained via text, checklists, screenshots, and videos.

3.4 Content Summary: How Will LNAPL Risk Change Over Time?

The Tier 1 module explains that the potential risk at many LNAPL sites is driven by the presence of benzene and describes how benzene removal over time from natural processes results in a decreasing risk associated with LNAPL for several common pathways at many sites. For the Tier 2 Module, an LNAPL dissolution calculator is provided so users can see how the chemical composition of LNAPL in groundwater might change over time. This dissolution calculation is based on Raoult's Law for partitioning of specific hydrocarbons between the LNAPL and aqueous phase over time as the LNAPL composition changes. The Tier 3 module highlights the API LNAPL Dissolution and Transport Screening Tool (LNAST) model using a video, checklist, and example output.

3.5 Content Summary: Will LNAPL Recovery Be Effective?

A simple graphic tool developed by the Texas Risk Reduction Program (TRRP) is used to illustrate the prospect of LNAPL recovery in the Tier 1 tool (TRRP, 2013) (Figure 3). It requires that users know the specific volume of LNAPL at a particular location and the hydraulic conductivity of the water-bearing unit in order to plot a point on the graph. Within the graph are curves for four common LNAPLs (gasoline, diesel, fuel oil #2, and fuel oil #4). If the plotted point is to the left of the appropriate curve, then LNAPL is not likely to be recoverable via pumping.

The Tier 2 module describes how the Multi-Site LNAPL Volume and Extent Model described above can also be used to estimate LNAPL recoverability by providing an estimate of the LNAPL transmissivity at a particular location if one knows the apparent thickness of LNAPL in a monitoring well and the soil characteristics of the water-bearing unit. According to guidance provided by the ITRC (2018), a key threshold for determining the feasibility of LNAPL recovery is the transmissivity value. Values above 0.0093 to 0.074 m^2/day indicate that LNAPL hydraulic recovery is likely to be cost-effective and efficient. However, if the calculated or measured LNAPL transmissivity falls below the lower value in this range, the chances of successful recovery through hydraulic methods decrease significantly. Wells with transmissivity values within this range are likely dominated by residual LNAPL. These values are based on considering various soil and LNAPL types according to the ITRC (2018). The Tier 3 module provides key resources, including four short videos, for accessing more complicated computer models and for obtaining LNAPL transmissivity data from field measurements.

3.6 Content Summary: How Can One Estimate NSZD?

The Tier 1 module emphasizes how NSZD is becoming an important factor in the CSM for LNAPL sites and how it can be used to manage LNAPL at impacted sites. Tier 1 also summarizes the key processes underlying NSZD at LNAPL sites and shows reported ranges from Garg et al. (2017) where the middle 50% of site wide NSZD rates fall between 6,600 and 26,000 liters of LNAPL being directly biodegraded per hectare per year. The Tier 2 Module provides calculators to convert between the myriad different types of NSZD rates (e.g., from gallons per acre per year in U.S. units to µmol per m^2 per sec for some research papers to liters of LNAPL biodegraded per hectare per year). Tier 3 provides access to a wide range of tools on how to measure and interpret NSZD at LNAPL-impacted sites, including videos on key NSZD measurement technologies.

4.0 DATA AVAILABILITY AND ACCESS TO THE CONCAWE LNAPL TOOLBOX

Option 1: Run the Toolbox by accessing the webpage on an internet browser using the URL *https://lnapltoolbox.concawe.eu/lnapl_toolbox/*. The recommended browsers are Google Chrome, Mozilla Firefox and Safari.

Option 2: Download the Toolbox at *https://github.com/concawe/LNAPL-Toolbox-* for use on your own computer or server. The required software are: R (version > 4.0.2); Python (version > 3.8). Since the Tool Box has been issued in April 2022, user feedback has mostly been positive, with the most issues related to the specific format of the layering input data for the Tool 1 Volume Calculator. Based on these comments, changes were made to the instructions and input file architecture for the input data.

5.0 CONCLUSIONS

A detailed web-based toolbox, written on the R-Shiny platform, was developed and as of April 2022 is freely available to help environmental consultants, regulators, and site owners better manage LNAPL-impacted sites. Key decision making support is provided to help estimate the volume of LNAPL in the subsurface, determine if LNAPL is likely to migrate further, understand how long the LNAPL might persist, evaluate if any risk associated with the

LNAPL will change over time, if LNAPL recovery systems will likely be effective, and recognize if Natural Source Zone Depletion is a key factor at their site. The Concawe LNAPL Toolbox is one of the first web-based LNAPL software tools designed specifically to help environmental professionals understand and manage LNAPL sites.

Acknowledgements

The authors would also like to acknowledge the contributions of Poonam Kulkarni of GSI Environmental and Brian Strasert and Hanna Podzorski while at GSI Environmental. In addition, the authors would like to acknowledge the Concawe STF-33 Task Force for conceiving and leading this project: Markus Hjort, Eleni Vaiopoulou, Patrick Eyraud, Richard Gill, Tim Greaves, Thomas Grosjean, Wayne Jones, Andras Medve, Jonathan Smith.

Competing Interest

The development of this tool was funded by Concawe. The authors declare no conflicts of interest.

REFERENCES

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.

Charbeneau, R., 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.

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

Garg, S., Newell, C. J., Kulkarni, P. R., King, D. C., Adamson, D. T., Renno, M. I., & Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Groundwater Monitoring and Remediation, 37(3), 62–81. https://doi.org/10.1111/gwmr.12219

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

ITRC, 2018. LNAPL-3: LNAPL Site Management – LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council. March 2018. https://lnapl-3.itrcweb.org Appendix B: Natural Source Zone Depletion (NSZD)

Mahler, N., Sale, T., & Lyverse, M., 2012. A Mass Balance Approach to Resolving LNAPL Stability. Ground Water, 50(6), 861–871. https://doi.org/10.1111/j.1745-6584.2012.00949.x

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.

Newell, C. J., Strasert, B., de Blanc, P., Kulkarni, P., Whitehead, K., Sackmann, B., & Podzorski, H., 2021. User manual for Concawe LNAPL toolbox. Concawe, Brussels, Belgium. Available at: https://www.concawe.eu/wp-content/uploads/Rpt_22-5.pdf.

Sale, T. C., Hopkins, H., & Kirkman, A., 2018. Managing Risk at LNAPL Sites - Frequently Asked Questions (2nd Edition). American Petroleum Institute. https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/lnapl-faqs

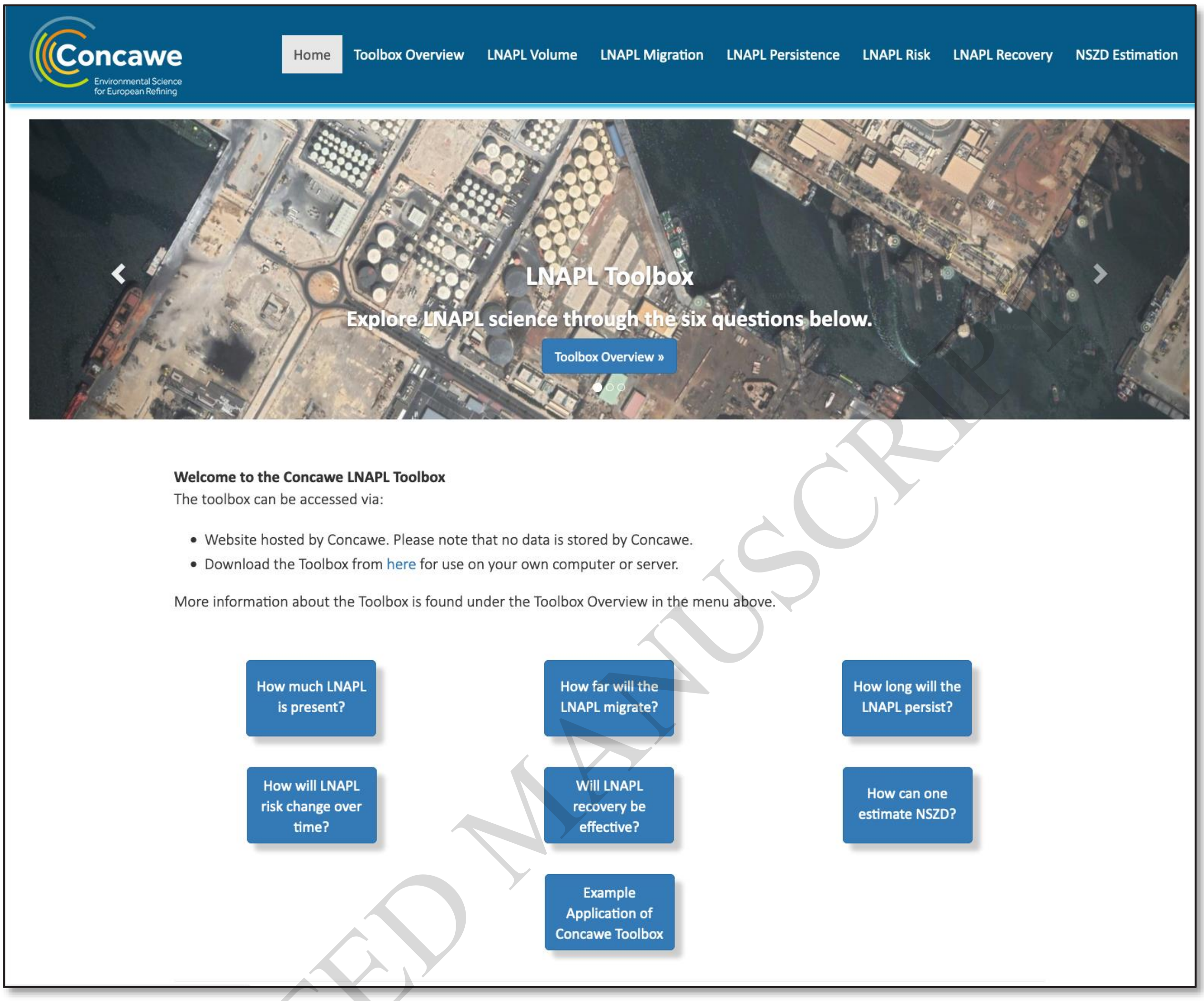
Strasert, B., Newell, C., de Blanc, P., Kulkarni, P., Whitehead, K., Sackmann, B., & Podzorski, H., 2021. Concawe LNAPL toolbox. Concawe, Brussels, Belgium. Available at: https://lnapltoolbox.concawe.eu/lnapl_toolbox/.

Texas Risk Reduction Program, 2013. Risk-Based NAPL Management, TRRP-32. Austin, Texas.

Tomlinson, D. W., Rivett, M. O., Wealthall, G. P., & Sweeney, R. E., 2017. Understanding complex LNAPL sites: Illustrated handbook of LNAPL transport and fate in the subsurface. Journal of Environmental Management, 204, 748-756.

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

FIGURES AND TABLES

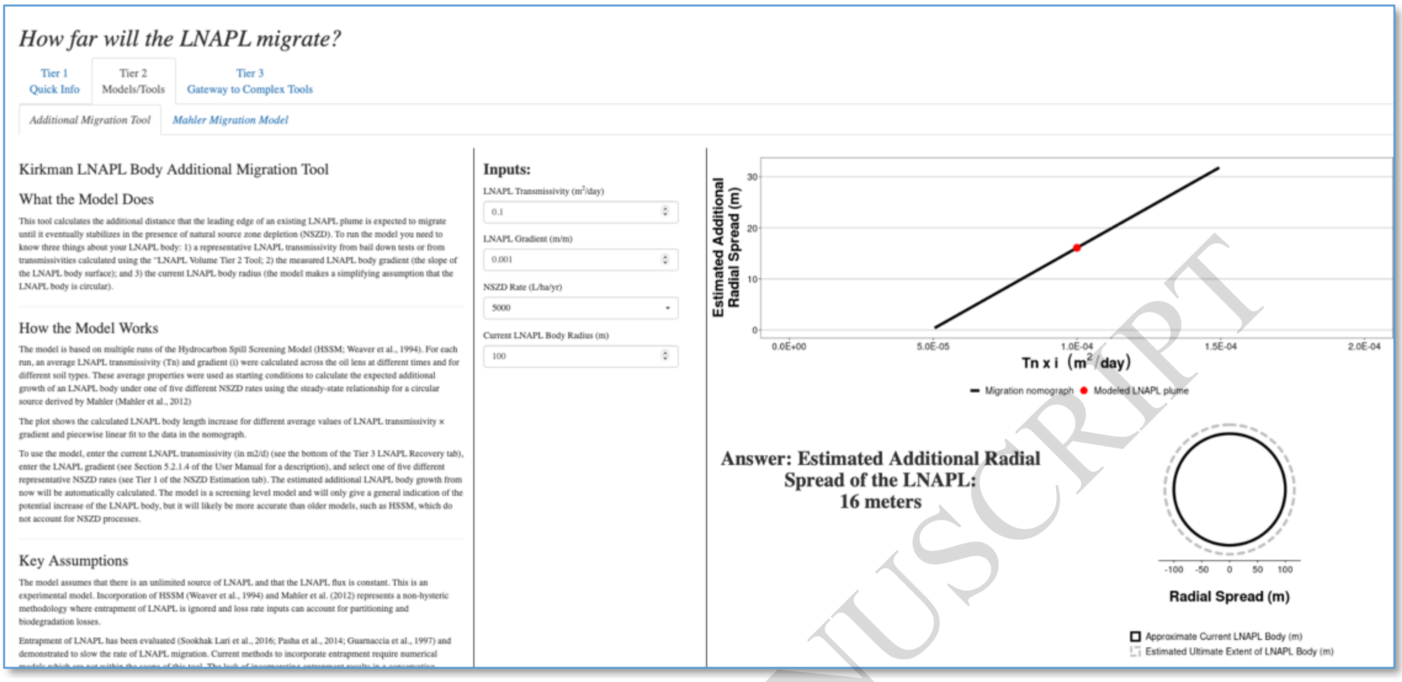


Welcome to the Concawe LNAPL Toolbox
The toolbox can be accessed via:

- Website hosted by Concawe. Please note that no data is stored by Concawe.
- Download the Toolbox from here for use on your own computer or server.

More information about the Toolbox is found under the Toolbox Overview in the menu above.

Figure 1. Concawe LNAPL Toolbox Landing Screen ((http://lnapltoolbox.concawe.eu/lnapl_toolbox/)



How far will the LNAPL migrate?

Kirkman LNAPL Body Additional Migration Tool

What the Model Does

This 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 know three things about your LNAPL body: 1) a representative LNAPL transmissivity from bail down tests or from transmissivities calculated using the "LNAPL Volume Tier 2 Tool; 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).

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 for different soil types. These average properties were used as starting conditions to calculate the expected additional growth of an LNAPL body under one of five different NSZD rates using the steady-state relationship for a circular source derived by Mahler (Mahler et al., 2012)

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

To use the model, enter the current LNAPL transmissivity (in m2/d) (see the bottom of the Tier 3 LNAPL Recovery tab), enter the LNAPL gradient (see Section 5.2.1.4 of the User Manual for a description), and select one of five different representative NSZD rates (see Tier 1 of the NSZD Estimation tab). The estimated additional LNAPL body growth from now will be automatically calculated. The model is a screening level model and will only give a general indication of the potential increase of the LNAPL body, but it will likely be more accurate than older models, such as HSSM, which do not account for NSZD processes.

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

Inputs:

LNAPL Transmissivity (m^2/day): 0.1

LNAPL Gradient (m/m): 0.001

NSZD Rate (L/ha/yr): 5000

Current LNAPL Body Radius (m): 100

Answer: Estimated Additional Radial Spread of the LNAPL: 16 meters

Figure 2: Screenshot of Kirkman Additional LNAPL Migration Tool in Concawe LNAPL Toolbox.

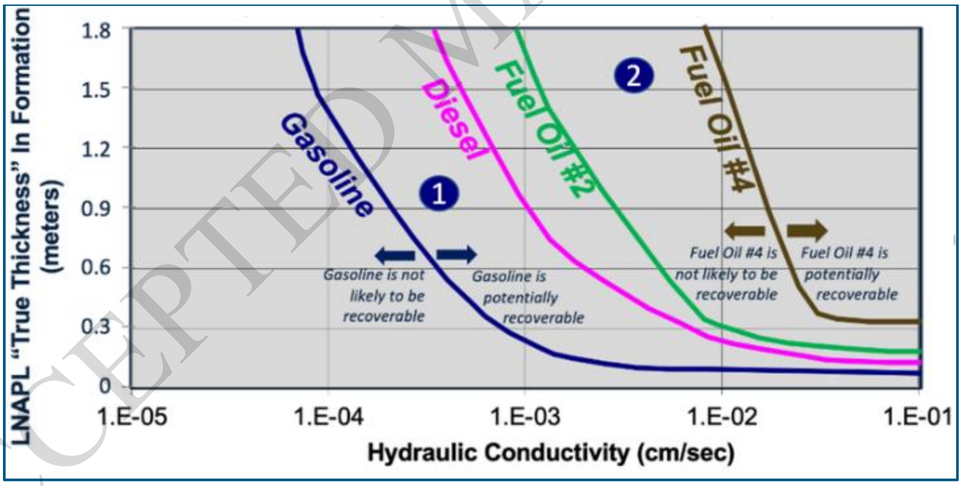


Figure 3. Texas Risk Reduction Program LNAPL Recoverability Tool. Source: Texas Commission on Environmental Quality (TRRP 2013)

Table 1. Concawe LNAPL Toolbox Organization and Structure (Source: Newell et al., 2021).

Key LNAPL Questions	Tier 1 Quick Info	Tier 2 Models / Tools	Tier 3 Gateway to Complex Tools

How much LNAPL is present?	Text, Simple Table and Graphic	NAPL Volume / Extent Tool	LDRM Resources and Video
How far will LNAPL migrate?	Text and Simple Graphic	LNAPL Additional Migration Tool and Mahler Migration Model	HSSM and UTCHEM Resources and Video
How long will LNAPL persist?	Text, Simple Graphic and Table	LNAPL Lifetime Calculator	LNAST and REMFuel Resources and Videos
How will LNAPL risk change over time?	Text and Simple Tables	LNAPL Dissolution Calculator	LNAST Resources and Video
Will LNAPL recovery be effective?	Text and Simple Graphics	LNAPL Transmissivity & Darcy Flux Calculator	Computer Modelling Resources
How can one estimate NSZD?	Text and Simple Graphic	NSZD Rate Converter, NSZD Temperature Enhancement Calculator	NSZD Resources and Videos

Notes: NSZD: Natural Source Zone Depletion. LDRM, HSSM, UTCHEM, LNAST are names of specific LNAPL computer models.

Table 2. Differences between the Multi-Site Volume and Extent Tool and LDRM (Source: Newell et al, 2021)

Multi-Site Volume and Extent Tool	**LDRM**
Estimates spatial variation of transmissivity and LNAPL volumes, while the LDRM does not.	Allows users to account for smear zones above and below the LNAPL lens, while the Multi-site tool does not.
Accesses a customizable soil properties database for different soil types, while the LDRM requires users to enter this information manually for every well.	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.
Estimates spatial variation of transmissivity and LNAPL volumes, while the LDRM does not.	Simulates LNAPL recovery for several kinds of systems, while the Multi-site tool does not simulate LNAPL recovery.
	Is limited to a 3-layer system, while the Multi-site tool considers up to 10 layers.
	Is limited to a single location, while the Multi-site tool calculates LNAPL properties at unlimited locations simultaneously.