How will LNAPL risk change over time? Tier 3

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.

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

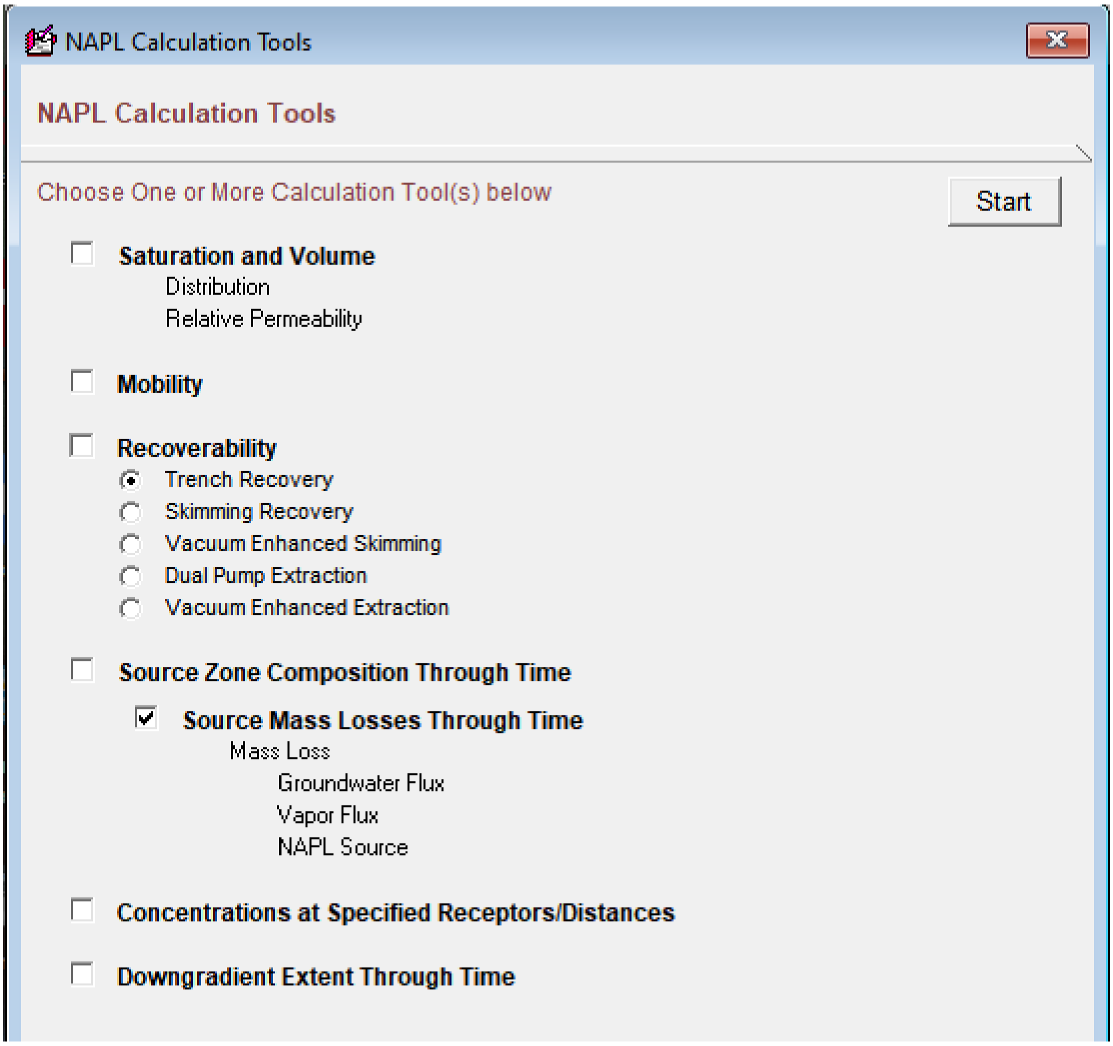
- LNAST is suite of calculation tools, information about LNAPL, and LNAPL parameter databases. LNAST focuses on LNAPL distribution and fate at the water table. The calculation tool part of LNAST:
  - Predicts LNAPL distribution, dissolution, and volatilization over time.
  - Calculates downgradient dissolved-phase 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.

Short Video

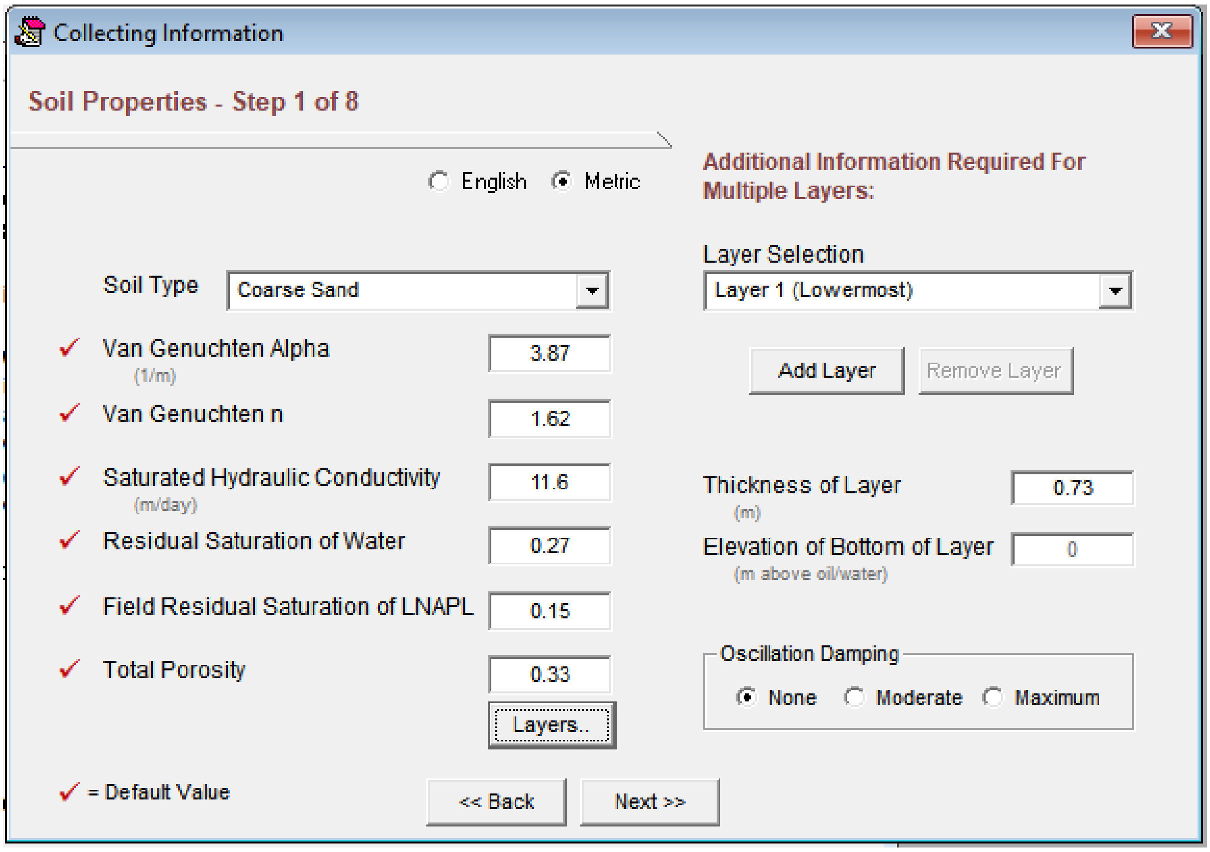
A short video to learn more about LNAST can be found here. [link to be added after Concawe review]

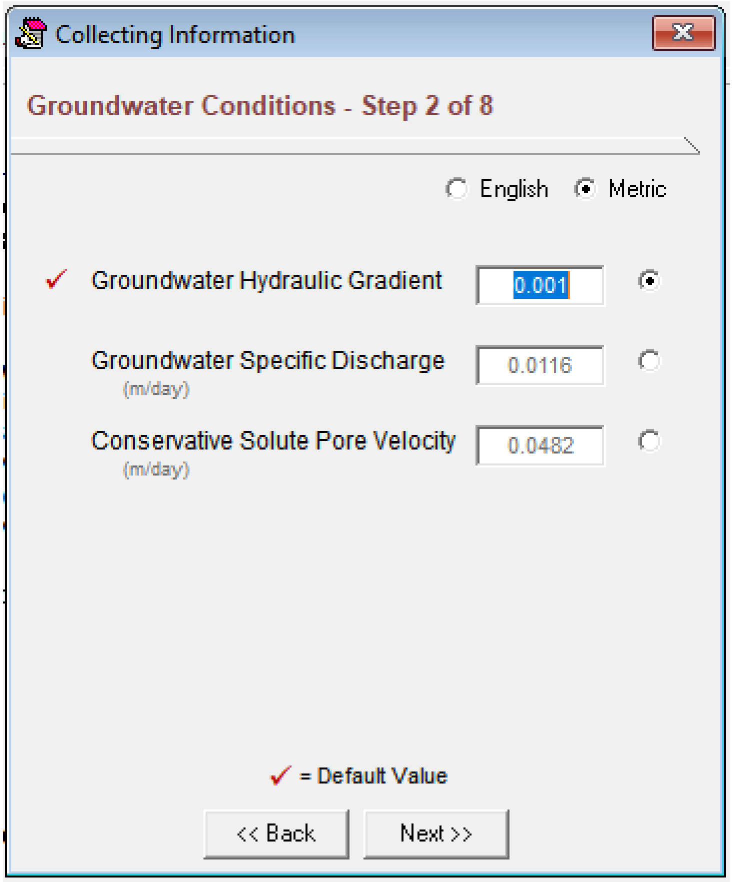
LNAST Input Data

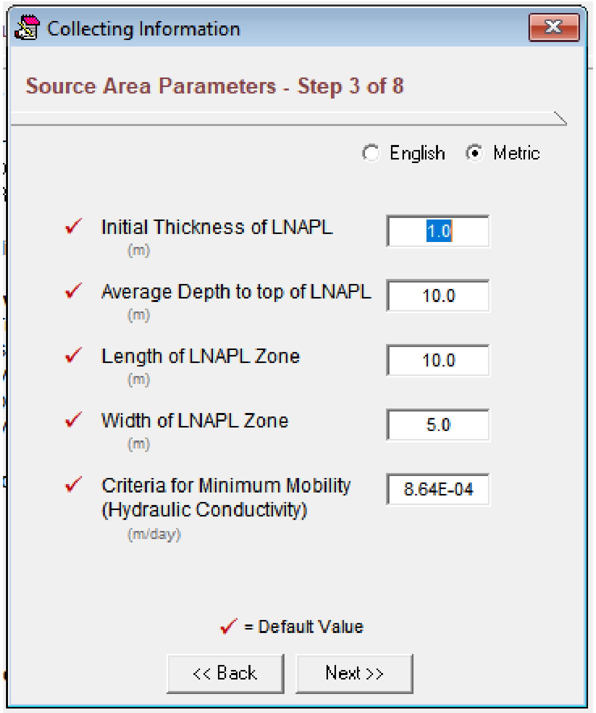
To use LNAST, the user first indicates the information desired from the tool:

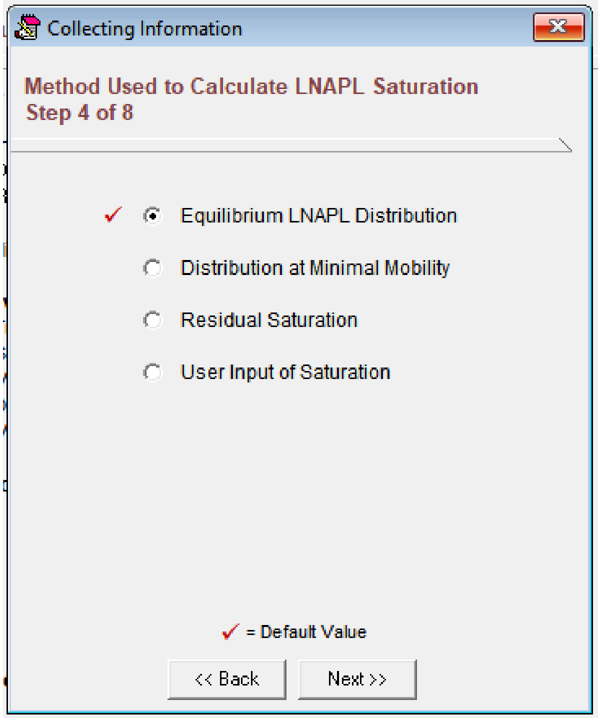


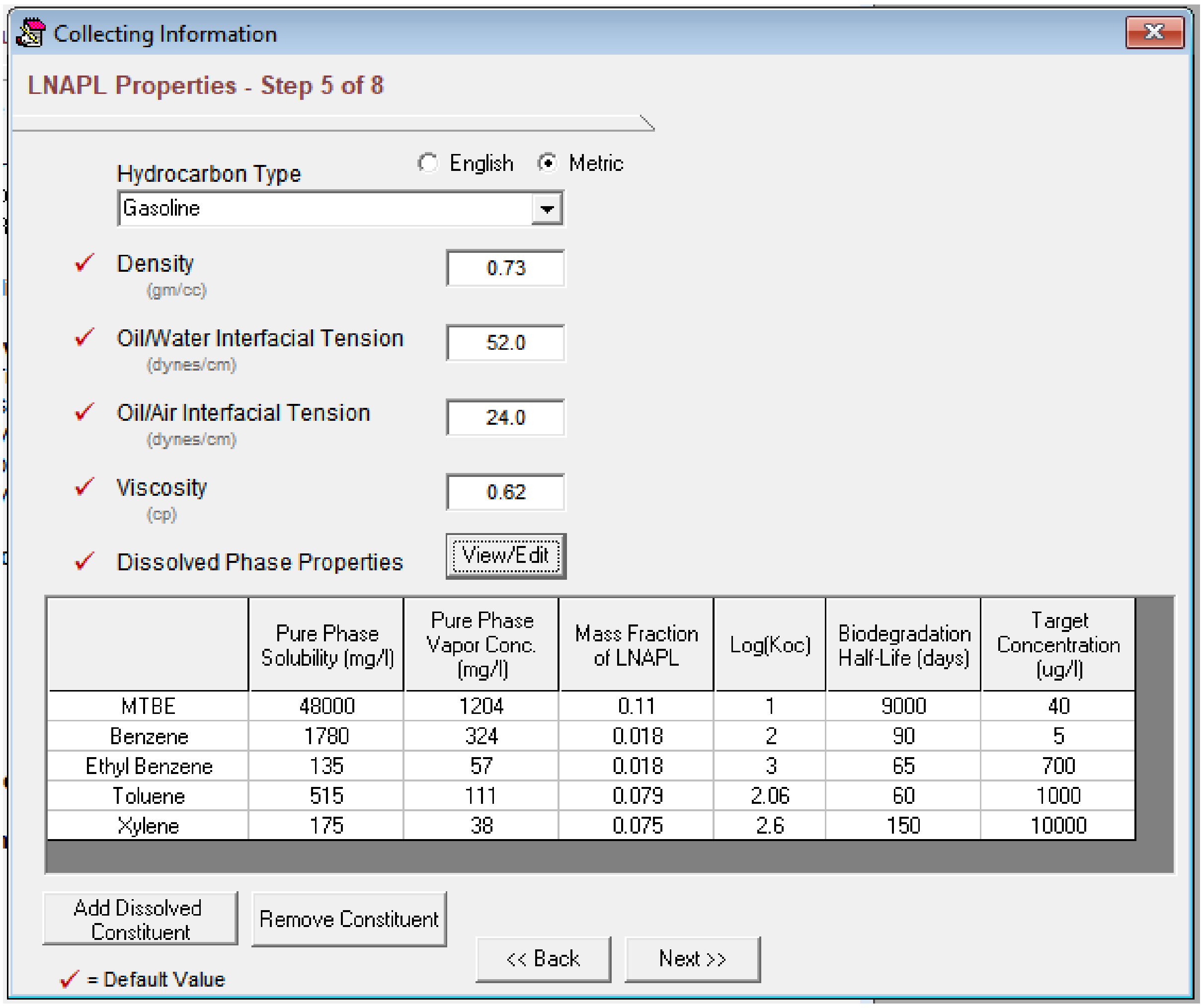
The tool then takes the user through a series of eight input screens to define soil properties, groundwater conditions, source area parameters, LNAPL properties, and solute transport.


Collecting Information
Soil Properties - Step 1 of 8
English
Metric
Soil Type
Coarse Sand
Van Genuchten Alpha
(1/m)
3.87
Van Genuchten n
1.62
Saturated Hydraulic Conductivity
(m/day)
11.6
Residual Saturation of Water
0.27
Field Residual Saturation of LNAPL
0.15
Total Porosity
0.33
Layers..
= Default Value
<< Back
Next >>
Additional Information Required For Multiple Layers:
Layer Selection
Layer 1 (Lowermost)
Add Layer
Remove Layer
Thickness of Layer
(m)
0.73
Elevation of Bottom of Layer
(m above oil/water)
0
Oscillation Damping
None
Moderate
Maximum

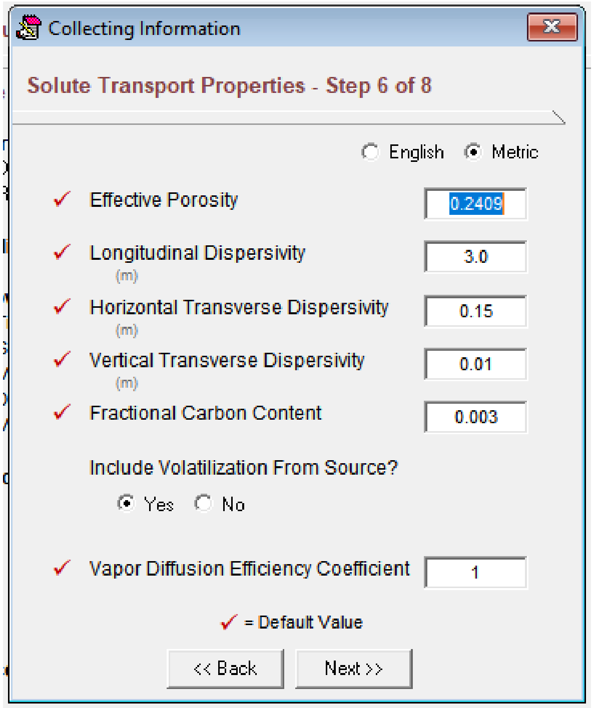

Collecting Information
Groundwater Conditions - Step 2 of 8
English
Metric
Groundwater Hydraulic Gradient
0.001
Groundwater Specific Discharge
(m/day)
0.0116
Conservative Solute Pore Velocity
(m/day)
0.0482
= Default Value
<< Back
Next >>

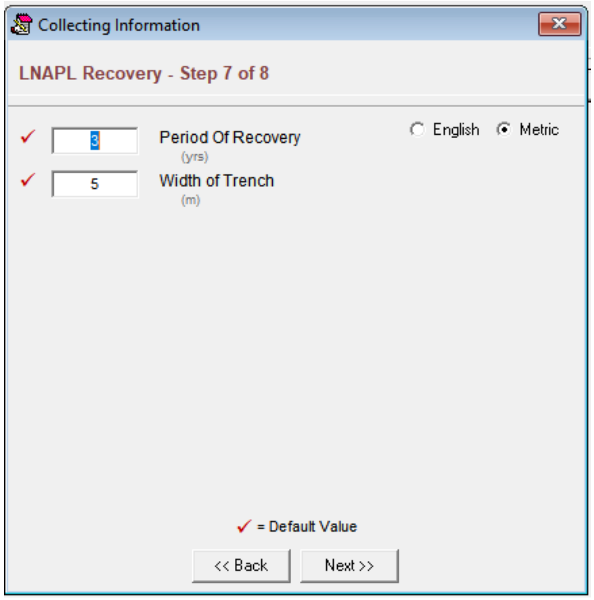


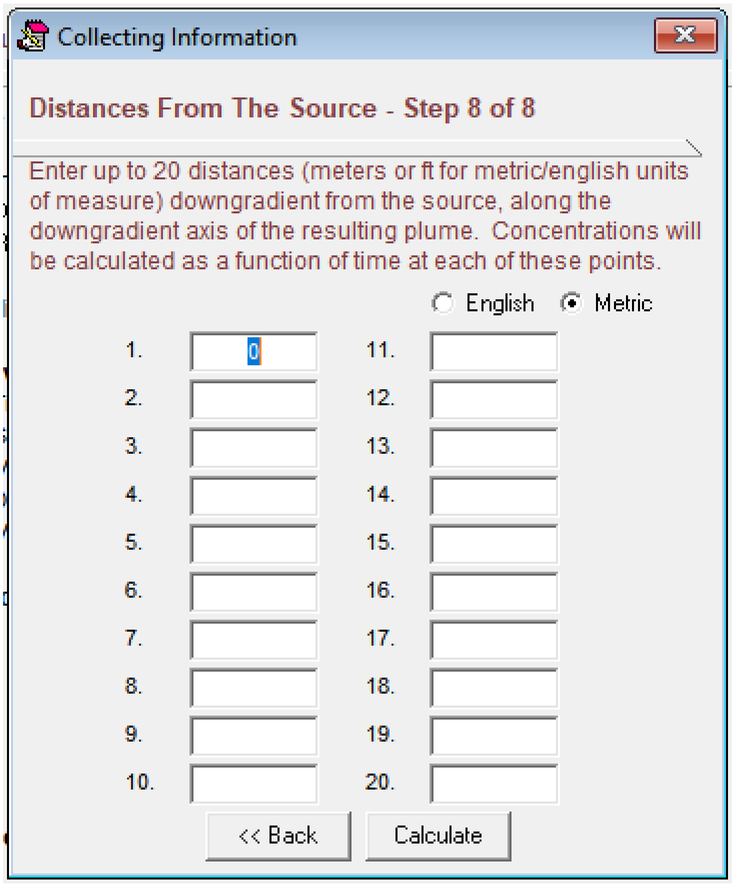




	Pure Phase Solubility (mg/l)	Pure Phase Vapor Conc. (mg/l)	Mass Fraction of LNAPL	Log(Koc)	Biodegradation Half-Life (days)	Target Concentration (ug/l)
MTBE	48000	1204	0.11	1	9000	40
Benzene	1780	324	0.018	2	90	5
Ethyl Benzene	135	57	0.018	3	65	700
Toluene	515	111	0.079	2.06	60	1000
Xylene	175	38	0.075	2.6	150	10000

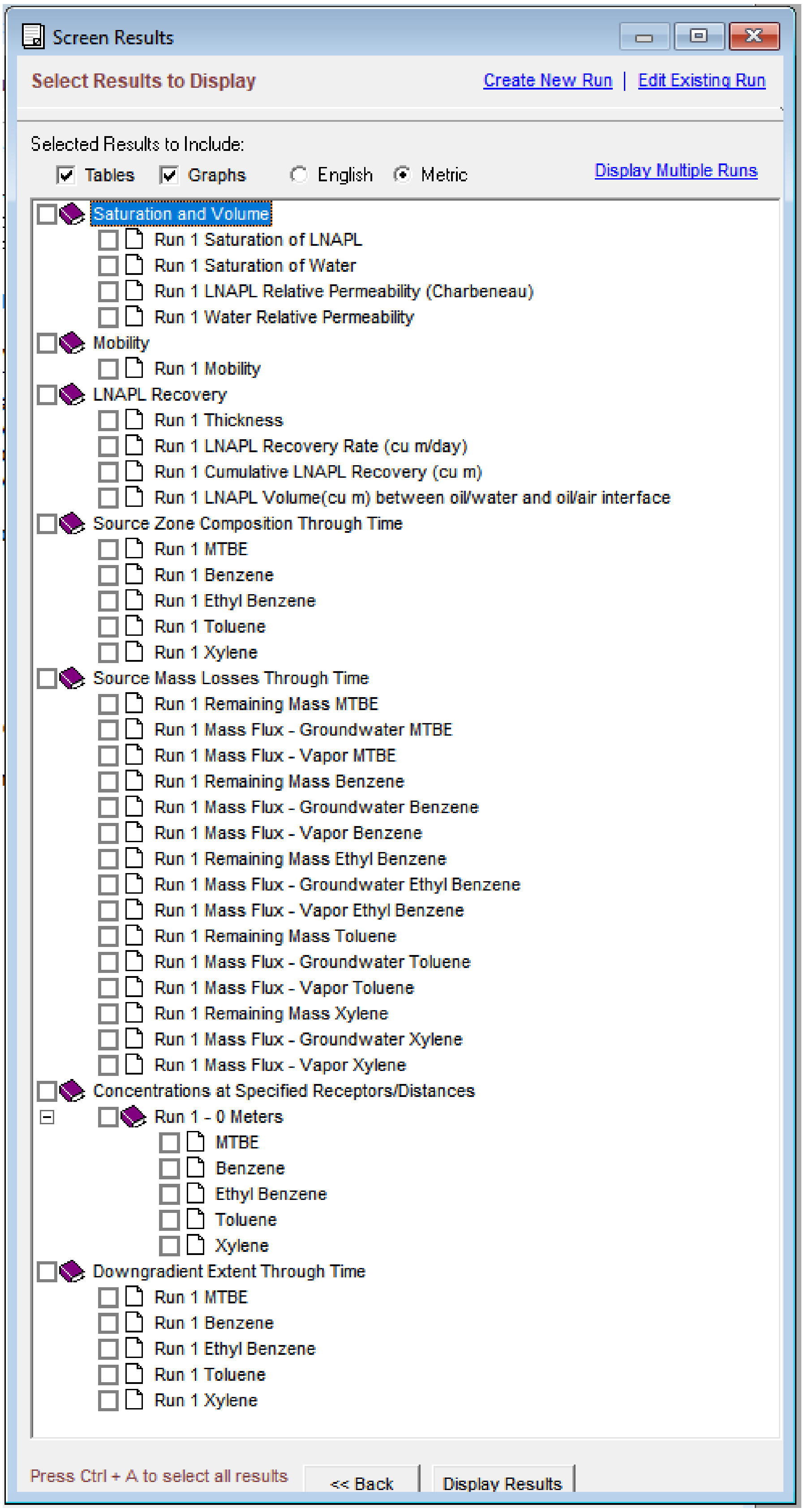

Collecting Information
Solute Transport Properties - Step 6 of 8
English
Metric
Effective Porosity
0.2409
Longitudinal Dispersivity
(m)
3.0
Horizontal Transverse Dispersivity
(m)
0.15
Vertical Transverse Dispersivity
(m)
0.01
Fractional Carbon Content
0.003
Include Volatilization From Source?
Yes
No
Vapor Diffusion Efficiency Coefficient
1
= Default Value
<< Back
Next >>


Collecting Information
LNAPL Recovery - Step 7 of 8
3
Period Of Recovery
(yrs)
English
Metric
5
Width of Trench
(m)
= Default Value
<< Back
Next >>

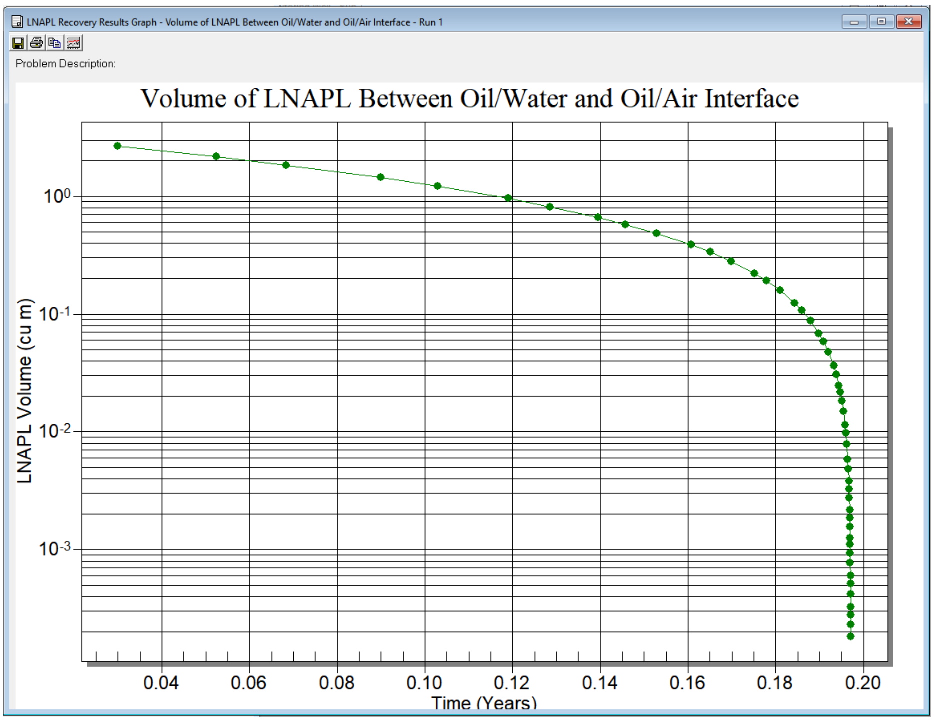

Collecting Information
Distances From The Source - Step 8 of 8
Enter up to 20 distances (meters or ft for metric/english units of measure) downgradient from the source, along the downgradient axis of the resulting plume. Concentrations will be calculated as a function of time at each of these points.
English
Metric
1.
0
2.
3.
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15.
16.
17.
18.
19.
20.
<< Back
Calculate

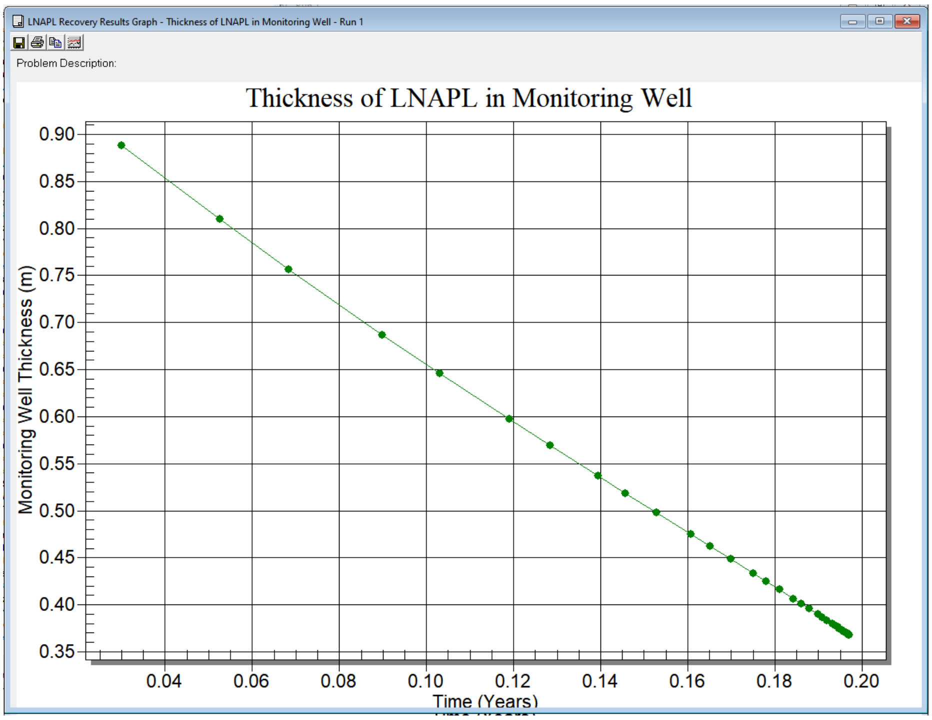
Example of LNAST Output Data

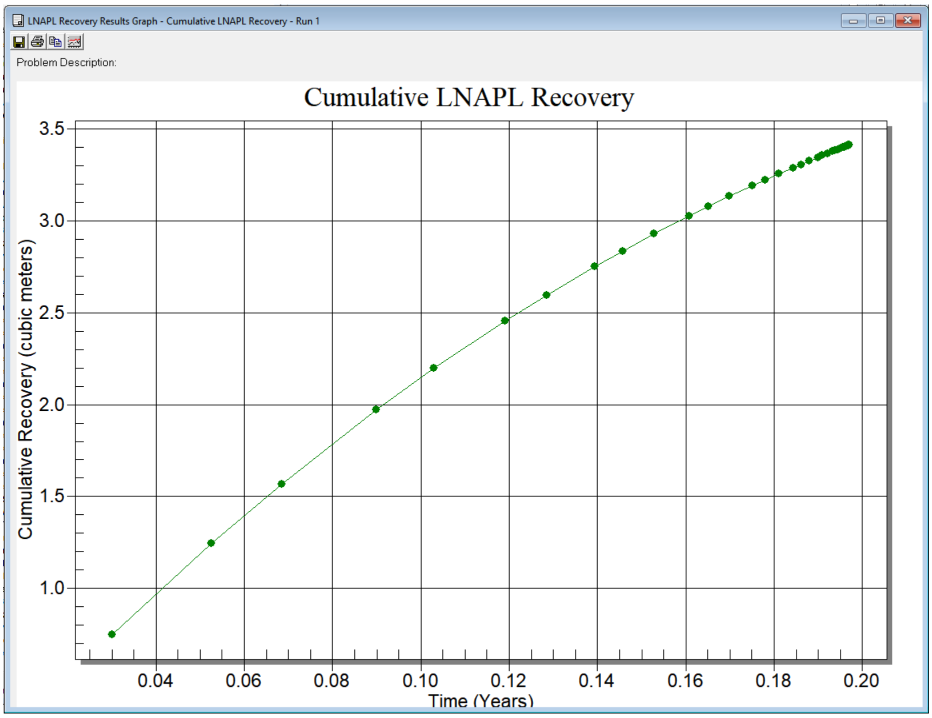
After performing the selected calculations, LNAST allows users to display results to the screen, create a report, or export the results.

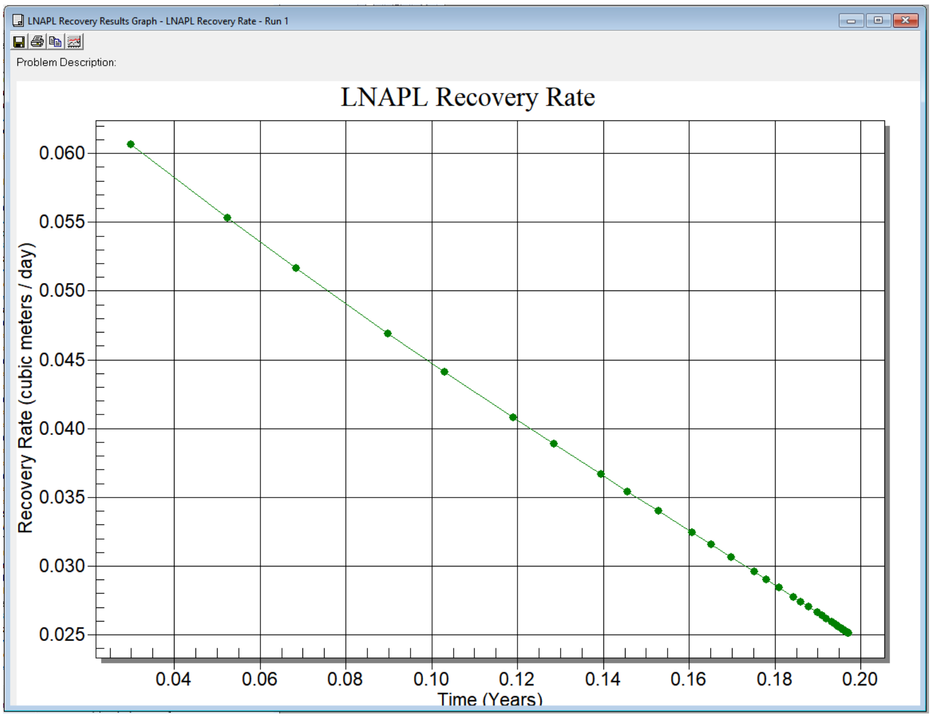


An example of key output for LNAPL recovery in a trench is shown below:









Description of Ng et al. (2014) LNAPL Model

- A reactive transport model of an LNAPL body was developed by Ng et al. to simulate a 1979 LNAPL release at what is now the National Crude Oil Spill Research Site.
- The model was based on extensive research conducted by the USGS and several universities to construct the model.
- As shown in the figure below developed by Garg et al. (2017), Ng et al. developed a mass balance around five “buckets”: BEX, toluene, short-chained alkanes, long-chained alkanes, and pre-NVDOC (non-volatile dissolved organic carbon).

- The figure shows the percent depleted of each bucket in 27 years (green values), the contribution to the NSZD rate (red values), the rate of biodegradation of each bucket (blue arrows), and an inhibition term (red arrows).

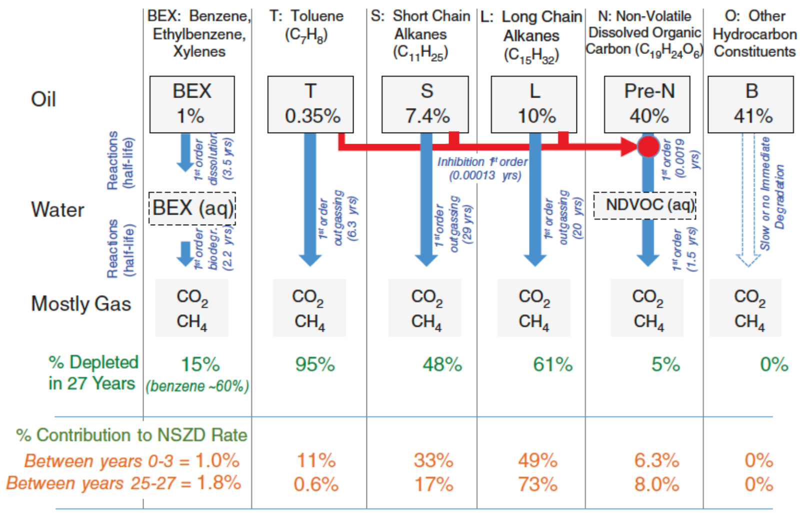


Figure 8. Simplified structure of Ng Model, showing five model constituent buckets (BEX: lumped benzene, ethylbenzene, xylenes; T: toluene; S: Shorted chained alkanes (represented by C11); L: long-chained alkanes (represented by C15); and Pre-N (pre-non-volatile dissolved organic carbon, representative molecular weight of 341 g/mole). BEX and NVDOC go through a dissolution step (modeled as a first-order process), then first-order decay in the aqueous phase; all other compounds are assumed to off from pores with LNAPL gas directly with the first-order decay constants shown in the blue text. These parameters were determined by Ng et al. (2015) from calibration to match observed composition change over a 27-year natural source zone depletion period. The percent degraded over the 27-year period, shown in green, is taken from Baedecker et al. (2011). Using data from the bottom panel of Figure 7, the approximate contribution to the total NSZD rate is shown in orange. Other hydrocarbon constituents included branched hydrocarbons, asphaltenes, and resins.

- The Ng et al. model was used to simulate LNAPL composition from the 1979 to the year 2079 as shown to the right (Garg et al., 2017).

- It assumed the "overall NSZD rate is approximately constant over time (pseudo-zero order), because the main contributors to NSZD, the short-chained and long-chained alkanes, are represented as a first-order decay rate where the biodegradation rate for these two constituent 'buckets' gets smaller over time. As they do, the inhibition effect on the pre-NVDOC bucket defined by Ng et al. (2014, 2015) diminishes and the pre-NVDOC starts to biodegrade and 'take up the slack' for the declining alkane degradation rate to produce a relatively constant biodegradation rate for much of the site history." (Garg et al., 2017).

- Overall, "the detailed reactive transport model developed by Ng et al. (2014 , 2015) was adapted to explore LNAPL composition change as a result of NSZD. This model suggests that methanogenic microorganisms consume different LNAPL constituents/chemical classes in a semi-sequential basis due to inhibition and other effects, which then can produce quasizero-order bulk NSZD rates over long time periods" (Garg et al., 2017).

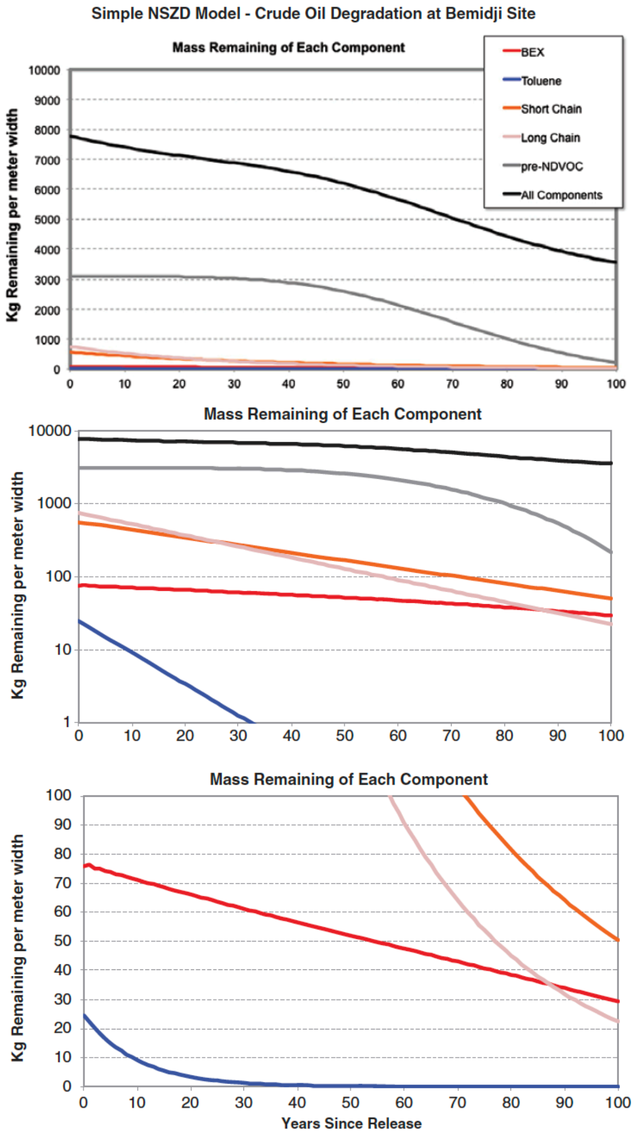
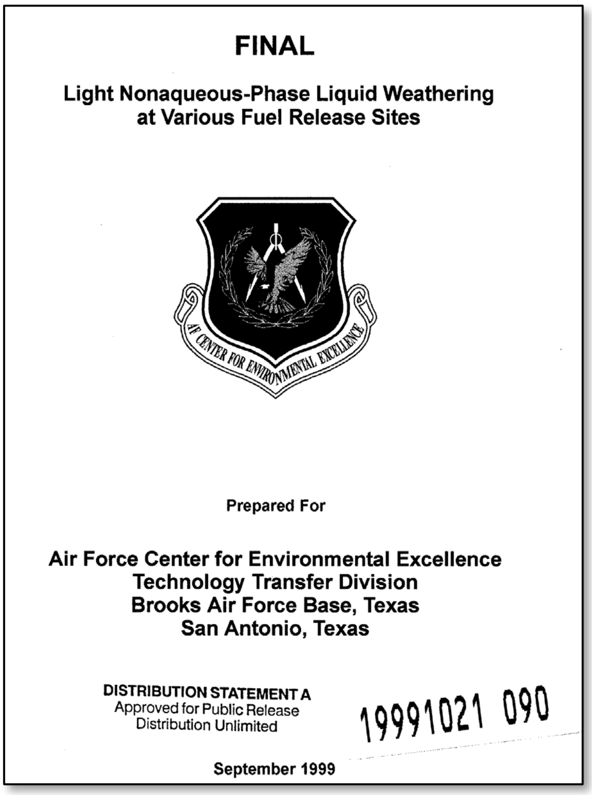


Figure 9. Mass remaining curves for five oil constituents using spreadsheet version of Ng Model for NSZD at Bemidji Site developed by the authors. "Short-Chain" and "Long Chain" indicates short- and long-chained alkanes respectively. All three graphs show same data but with different y-axes. An overall quasi-zero-order rate can be elucidated from the black line (all components) in the top panel, which represents the sum of first-order reactions of different rates for the various "buckets," and the effect of inhibition on pre-NVDOC biodegradation.

Parsons Fuel LNAPL Weathering Study



FINAL

Light Nonaqueous-Phase Liquid Weathering at Various Fuel Release Sites

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San Antonio, Texas

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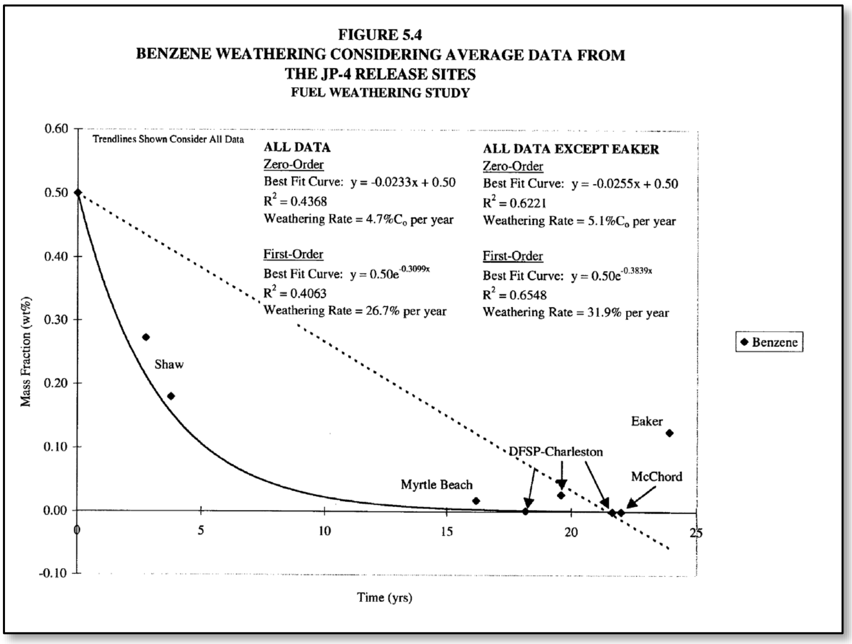
- Study of 12 LNAPL sites where data on concentration of BTEX constituents in LNAPL (as weight percent) vs. time (over the span of several years) in LNAPL source zones was compiled (Parsons et al., 2003). Jet fuel (JP-4) was the LNAPL found at most of these sites.
- "Free-phase fuel BTEX weathering rates will vary from site to site and are influenced by many factors including spill age, the relative solubility of individual compounds, free product geometry, and the rate at which groundwater and precipitation contacts LNAPL."
- "…the average total BTEX, first-order weathering rate for five JP-4 sites is approximately 16 %/yr. Based on all of the data collected, this appears to be a reasonable default value for estimating total BTEX weathering from JP-4 LNAPL."
- "As predicted by their relatively high solubilities, benzene and toluene exhibit higher weathering rates than ethylbenzene and xylenes. Because benzene is a known human carcinogen with a federal MCL of 5 µg/L, benzene weathering rates will generally determine the timeframe for fuel spill remediation." "Based on Figure 5.4, the average benzene first-order weathering rate for five JP-4 sites is approximately 26 %/yr. Based on all of the data collected, this appears to be a reasonable default value for estimating benzene weathering from JP-4 LNAPL."



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 modeling 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.