Naval Facilities Engineering Systems Command

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Vadose Zone Model Technical Memorandum
Red Hill Bulk Fuel Storage Facility

JBPHH, O‘ahu, Hawai‘i

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Acronyms and Abbreviations

AGU	American Geophysical Union
CF&T	contaminant fate and transport
cm	centimeters
d	days
DTW	depth to water
ft	foot/feet
g	grams
gal	gallons
JP-5	Jet Propellant-5
JP-8	Jet Propellant-8
L	liters
LNAPL	light nonaqueous-phase liquid
m	meters
mg	milligrams
NSZD	natural source-zone depletion
TPH-d	total petroleum hydrocarbons – diesel range
TPH-o	total petroleum hydrocarbons – residual oil range
TRRP	Texas Risk Reduction Program
VZM	vadose zone model

1.0 Summary

The United States Navy has been directed to create a groundwater flow and contaminant fate and transport (CF&T) model to simulate the impact of a potential release of light nonaqueous-phase liquid (LNAPL) during defueling of storage tanks in the area of Red Hill, Oʻahu, Hawaiʻi. To simulate the fate and transport of LNAPL constituents in groundwater, a source term must be developed that specifies the extent of the LNAPL accumulation on the water table and the concentrations of LNAPL constituents that dissolve into groundwater. GSI Environmental Inc., in coordination with AECOM Technical Services Inc., has developed a vadose zone model (VZM) to create the source terms for the CF&T model for several different release scenarios. This technical memorandum describes the development and use of the VZM.

The VZM described in this document represents the best current interpretation of the local subsurface characteristics that control the extent of LNAPL in the vadose zone. Because modeling is usually an iterative process in which new data are analyzed and old data are reassessed, this heuristic model is subject to change as better and/or more detailed information is analyzed.

The VZM consists of two parts that quantify the source term, or boundary condition characteristics, for the CF&T model: 1) a mass balance model to quantify the size and shape of an LNAPL lens on the water table, and 2) a partitioning module that calculates LNAPL chemical constituent concentrations in groundwater within the LNAPL lens. Because the mass balance model relies on professional judgment for assumptions and model parameters, the mass balance model is called the “heuristic model” to emphasize that it incorporates elements of professional judgment. The calculations of the VZM heuristic model and partitioning module are programmed into a Microsoft Excel spreadsheet, which facilitates the rapid evaluation of many different scenarios and parameter sets.

For a given LNAPL release volume and location, the heuristic model calculates the volume of LNAPL retained in the vadose zone. LNAPL not retained in the vadose zone is assumed to form an LNAPL lens on the water table, where it spreads over an area with a uniform thickness and saturation. The extent of the LNAPL spreading depends on the thickness and saturation values specified by the user. The heuristic model provides input to the chemical partitioning module that calculates the concentration of two LNAPL constituents in groundwater: total petroleum hydrocarbons – diesel range (TPH-d) and total petroleum hydrocarbons – residual oil range (TPH-o). Concentrations of other chemical constituents identified by the user may also be calculated with the partitioning module.

Three historical release scenarios were simulated to constrain the heuristic model predictions based on empirical observations, and twelve hypothetical release scenarios were modeled to estimate the impacts of combinations of three potential release volumes at four potential release locations. With the exception of the January 2014 historical release, the LNAPL released in all scenarios was assumed to be Jet Propellant-5 (JP-5) fuel, which does not typically contain significant soluble TPH-o components. The fuel released in January 2014 was Jet Propellant-8 (JP-8)/F-24 instead of JP-5. The modeled scenarios, the resulting LNAPL lens sizes, and the initial concentrations of TPH-d in groundwater within the LNAPL lens for each scenario are provided in Table 1. The results provided in Table 1 are for the specific set of initial parameters currently used in the model as shown in Figures 1 through 6. These results will change based on the sensitivity study and calibration of the CF&T model.

2.0 Model Conceptualization and Key Assumptions

In the heuristic model conceptualization, LNAPL is instantaneously released uniformly over a specified area and migrates downward within the vadose zone. Several structural features including the strike and dip of underlying rocks, as well as rock fractures and void spaces with unknown orientation, numerous layers of clinker, potential presence of lava tubes, and the degree of horizontal to vertical anisotropy can all cause the path of LNAPL moving through the rock to be unpredictable. In addition, within the vadose zone, some LNAPL can be trapped in fractures, pools, lava tubes, and unconsolidated material. As a result of all these unpredictable effects, transport pathways through the vadose are not expressly modeled, and it is simply acknowledged that the LNAPL migrates downward through the vadose zone, which is consistent with what occurred in November 2021. However, the model is flexible in that “landing points” for the LNAPL on the groundwater table can be adjusted to match any given scenario, and the model can estimate a source term for CF&T modeling of that scenario.

The amount of LNAPL trapped in the vadose zone depends on an assumed vadose zone residual LNAPL saturation specified by the user. Residual LNAPL saturations in vadose zone soils vary widely. Typical residual saturations for middle distillates range from 0.02 for coarse gravel to 0.1 for silt or fine sand (Brost and DeVaull. 2000). In lava rock environments such as the Red Hill area, residual saturations are expected to vary much more widely than in unconsolidated soils. For example, residual saturations could approach 1 where LNAPL is retained in the open channels of lava tubes, or be less than 0.01 in cemented clinker. Therefore, for this VZM, the vadose zone LNAPL saturation is not based on an assumption of any specific subsurface geologic architecture or calculations of capillary retention. Instead, the vadose zone LNAPL saturation is simply an estimate of the fraction of the pore space that will retain LNAPL, and is based on the professional judgment of the user.

With this LNAPL distribution conceptualization, a much wider range of potential residual saturations will be considered for the VZM and the CF&T model boundary conditions. Although a wide range of residual saturations are explored in the sensitivity study, initial residual saturations are assumed to be relatively small, a conservative assumption that results in more LNAPL reaching the water table.

Except for its use to determine the volume of LNAPL retained in the vadose zone, the release area at the surface does not affect the size of the lens formed by LNAPL on the water table, which depends on the LNAPL lens characteristics specified by the user.

The volume of the released LNAPL that is not retained in the vadose zone reaches the water table, where it forms a lens on the groundwater. The LNAPL lens is of uniform thickness and uniform LNAPL saturation. Although an LNAPL lens that forms on the water table will contain different proportions of air, water, and LNAPL, the air phase is ignored in the heuristic model for simplifying purposes, such that only LNAPL and water phases are assumed to exist in the LNAPL lens. This assumption allows the saturated form of Darcy’s Law to be used in the partitioning module, greatly simplifying the calculations, and resulting in higher aqueous phase concentrations compared to a model in which partitioning into an air phase is considered.

The area of the LNAPL lens is calculated from the volume of LNAPL that reaches the water table, the saturation of LNAPL assumed to exist in the LNAPL lens, and the assumed LNAPL lens thickness. Although the LNAPL saturation and lens thickness will vary across the LNAPL lens area, they are assumed to be uniform in this simple model, so that the specified values represent spatial averages across the lens area. It is assumed that small releases will create relatively thin LNAPL lenses with low LNAPL saturations, while large releases will create thick LNAPL lenses with relatively large LNAPL saturations. Average uniform LNAPL lens saturations and thicknesses are based on engineering judgment and are specified by the user. The use of average values for LNAPL lens area, saturation, and thickness eliminates the need to specify or calculate the spatial and temporal variability of these LNAPL lens characteristics. This simplification of LNAPL lens geometry is considered sufficient for the simple mass balance heuristic model described here because the model calculations are based on uniform conditions that cannot incorporate spatial variability of subsurface characteristics.

The shape of the LNAPL lens on the water table is not specified by the heuristic model. The model simply reports the area of the LNAPL lens. For informational purposes, the model reports a radius of the LNAPL lens based on an assumption of a circular lens shape, but any shape of the LNAPL lens may be assumed for use as a CF&T model boundary condition. By default, the shape of the LNAPL lens is assumed to be a square for the calculation of LNAPL constituent dissolution in the partitioning module.

In the partitioning module of the VZM, LNAPL constituents dissolve into groundwater that flows through the LNAPL lens based on their effective solubilities. As the more soluble LNAPL constituents dissolve, the LNAPL becomes enriched in the less soluble LNAPL constituents, and the individual constituent effective solubilities change with the changing LNAPL composition. The partitioning module tracks both the changes in constituent concentrations in groundwater and LNAPL, and the volume of LNAPL remaining in the LNAPL lens over time. Eventually, all of the LNAPL is dissolved, and the constituent concentrations in the lens become zero, although the dissolution of the LNAPL could take a very long time if the LNAPL contains relatively insoluble constituents.

For the VZM partitioning module, dissolution is the only LNAPL depletion mechanism. In reality, volatilization, biodegradation, adsorption, and other natural source-zone depletion (NSZD) processes will also cause LNAPL depletion. Therefore, the heuristic model is conservative in that it overpredicts the persistence of LNAPL constituents in the groundwater source area.

The rate of LNAPL constituent concentration changes and LNAPL depletion depend on the rate of groundwater flow through the LNAPL lens. The partitioning module also includes a factor to account for the lack of uniform distribution of LNAPL (a “sweep efficiency” factor), and a factor to account for water reductions in water hydraulic conductivity as a function of LNAPL presence. Both these factors are functions of the LNAPL saturation in the LNAPL lens.

The model conceptualization and calculations in this VZM, which are partially based on parameters determined by professional judgment, represent the best current estimates of the range of subsurface conditions expected to be encountered at Red Hill. Uncertainty in parameters, many of which have significant effects on VZM calculations, is inherent in a model that relies on professional judgment. To quantify the uncertainty, and determine parameter sets that produce the most realistic results, a sensitivity study will be performed. The sensitivity study will vary key input parameters over a large range with the aim of producing a histogram of likely outcomes in terms of LNAPL lens size. A set of parameters that produces the most likely LNAPL lens size will be used to develop the boundary conditions for the CF&T model.

3.0 Model Input

VZM input parameters are specified on tabs in the model Excel spreadsheet. The model relies on primary inputs, which are input parameters or specified values entered by the user, and secondary inputs, which are calculated values based on the primary input.

Primary inputs are entered on each spreadsheet tab in the yellow-shaded cells. Blue-shaded cells are lookup values from other spreadsheet tabs that contain primary or secondary inputs. These lookup values may be overwritten by the user.

3.1 Main Tab

A screenshot of the Main tab of the VZM spreadsheet is shown on Figure 1. On the Main tab, the user specifies the release scenario and the groundwater hydraulic gradient magnitude. Fifteen release scenarios can be selected, corresponding to the three historical LNAPL releases and the twelve hypothetical releases listed on the Release Info tab (described in the next section). The groundwater gradient is used by the partitioning module. Several model parameters are calculated based on the selection of the release scenario. Parameters that depend on the selection of the release scenario include the following:

- Average residual saturation of the vadose zone;
- Average porosity of the vadose zone;
- Release location;
- Release volume;
- Release area;
- Depth to the water table at the release location;
- Thickness of the LNAPL lens;
- Porosity of the saturated zone;
- LNAPL saturation in the LNAPL lens; and,
- Hydraulic conductivity of the saturated zone (used in the partitioning module).

The sources of these parameter values are identified in the other tabs from which the values are obtained. The user is not limited to the fifteen release scenarios, and may overwrite parameters in the blue-shaded input cells if desired. If the lookup values of these parameters associated with the release scenario are overwritten by the user, the lookup formulas may be restored to the blue cells by clicking the “Restore Lookup Formulas” button on the main tab.

3.2 Release Info Tab

On the Release Info tab shown on Figure 2, the user specifies the type of LNAPL released, the location of the release, the volume of the release, and the area of the release at the ground surface. These values are used in subsequent model calculations. Default average LNAPL lens saturation and LNAPL lens thickness are also shown on this tab based on the volume of release. These parameters can be changed by the user if desired.

3.3 Location Info Tab

Key inputs on the Location Info tab include the following:

- Depth to water (DTW) at each release location;
- Volume fraction of rock types (‘A‘ā, pahoehoe, clinker, and saprolite) at each location;
- Calculated vadose zone porosity based on the rock types at the location;
- Calculated hydraulic conductivity based on the rock types at the location; and,
- Average residual LNAPL volumetric content based on the rock types at the location.

The average porosity, hydraulic conductivity, and residual LNAPL volumetric content at each location are weighted averages of these properties for each rock type. The values of these parameters for each rock type are specified on the Hydrogeologic Info tab. A screenshot of the Location Info tab is shown on Figure 3.

3.4 Hydrogeologic Info Tab

Properties of each rock type used to calculate average rock properties at each location are entered in the Hydrogeologic Info tab. A screenshot of the Hydrogeologic Info tab is shown on Figure 4. For each rock type, the user specifies an estimated total porosity, hydraulic conductivity, and residual vadose zone LNAPL saturation. The residual volumetric content used in the calculation of the volume of LNAPL retained in the vadose zone is also calculated on this tab for each rock type.

3.5 Fuel Info Tab

LNAPL properties are specified on the Fuel Info tab, shown on Figure 5. Three fuel types are currently listed: JP-5, JP-8 (also known as “F-24”), and Marine Diesel (also known as “F-76”). For each fuel type, an estimated specific gravity and molecular weight are specified. These parameters are used in the partitioning calculations. For each fuel type, the insoluble component of the fuel is indicated, and properties of this insoluble fraction are specified in the Chem Props (chemical properties) tab. The volumetric fraction of the two LNAPL constituents modeled, TPH-d and TPH-o, are also specified for each fuel type, and the properties of these two LNAPL constituents are entered at the Chem Props tab.

3.6 Partitioning Tab

The concentration of soluble LNAPL constituents in groundwater flowing through the LNAPL lens are calculated on the Partitioning tab, shown on Figure 6. In the first section on this tab, “General Parameters,” the user indicates whether LNAPL presence in the LNAPL lens is assumed to affect relative permeability, and whether the calculated equilibrium concentrations should be diluted because of only partial contact of the groundwater with the LNAPL (sweep efficiency effects). Entering a value of 1 for these flags reduces the concentrations of constituents in the groundwater, causing the LNAPL to persist for a longer time.

In the "LNAPL Constituent Parameters and Initial Values" section of the Partitioning tab, the user specifies what soluble constituents are present in the LNAPL. The default constituents are TPH-d and TPH-o, although volume fractions of other constituents can also be specified. Each constituent's molecular weight, solubility, and density are obtained from the Chem Props tab. The final constituent, which comprises the more insoluble part of the LNAPL, is obtained from the Chem Props tab. The volume fractions of TPH-d and TPH-o are also obtained from the Fuel Info tab.

The next section of the Partitioning tab contains calculations of input parameters needed for the partitioning calculations. The partitioning calculations are performed below this section at the bottom of the sheet. For each time interval, the concentration of constituents in groundwater in the source zone, the concentrations remaining in the LNAPL, and the remaining LNAPL volume are calculated.

The time increment for the partitioning module can be changed on the main heuristic model tab. If the timestep is too large, the solution may become unstable and the model will not yield accurate calculations or will produce errors in some spreadsheet cells. For LNAPLs that contain mostly insoluble components, longer time increments will not significantly affect the calculated concentrations. For the LNAPL calculations at Red Hill where constituents are mostly TPH-d and TPH-o, a time increment of 5–50 days is suggested. However, this time increment range is not guaranteed to result in model calculation stability, and the user must inspect the model results to evaluate how the time increment affects the results with the specified set of parameters.

3.7 Chem Props Tab

Chemical properties, including molecular weight, solubility, and density of each constituent are contained in the Chem Props tab. The data in columns 1 through 13 in the Chem Props tab are sourced from the Texas Risk Reduction Program (TRRP) spreadsheets (TCEQ 2023). Users must enter the density in column 14 for constituents that are part of the LNAPL but for which no density is specified. Molecular weights, solubilities, and densities of constituents not included in the TRRP database have been entered starting on row 710 of the Chem Props tab. Additional constituents may be added to the database as needed.

4.0 Model Calculations

The definition of variables used in the VZM calculations are defined in the table below. The example calculations provided for the heuristic mass balance model are for the example input shown on Figure 1.

Variable	Description	Dimensions or Units
Heuristic model mass balance calculations:		
A_{lens}	Area of LNAPL lens on water table	ft^2
A_{rel}	LNAPL release area at surface	square feet (ft^2)
b_{lens}	Thickness of LNAPL lens on water table	ft

Variable	**Description**	**Dimensions or Units**
DTW	Depth to water table	feet (ft)
n_{sat}	Porosity of saturated zone	ft^3 pores per ft^3 bulk volume
n_{vad}	Porosity in vadose zone	ft^3 pores per ft^3 total bulk volume
$S_{N,sat}$	LNAPL saturation in the LNAPL lens	ft^3 LNAPL per ft^3 pores
$S_{Nr,vad}$	Residual saturation of LNAPL in vadose zone	ft^3 LNAPL per ft^3 pores
$V_{N,sat}$	Volume of LNAPL reaching water table (saturated zone)	ft^3 LNAPL
$V_{N,vad}$	Volume of LNAPL retained in vadose zone	ft^3 LNAPL
$V_{p,vad}$	Pore volume of affected vadose zone	ft^3
V_{rel}	Volume of LNAPL released	cubic feet (ft^3) of LNAPL
V_{vad}	Bulk volume of affected vadose zone	ft^3 pores
$\theta_{N,sat}$	Volumetric content of LNAPL in the LNAPL lens on the water table	ft^3 LNAPL per ft^3 bulk volume
Partitioning model calculations:		
Δt	Time step	d
b	Average thickness of LNAPL lens	m
f_{sweep}	Sweep efficiency factor	dimensionless
i	Hydraulic gradient	dimensionless
K	Hydraulic conductivity	m/d
k_{rel}	Water relative permeability	m^2
n	Number of constituents in LNAPL	
N	Moles	moles
N_T	Total moles	moles
q	Specific discharge (Darcy flux)	m/d
Q	Volumetric flow rate of groundwater through LNAPL lens	m^3/d
S	Solubility of pure LNAPL component	mg/L
Se	Effective solubility	mg/L

Variable	Description	Dimensions or Units
V_N	Volume of LNAPL	m^3
w	Width of LNAPL lens	m
x	Mole fraction	moles of constituent i/total moles
z	Mass fraction	mass of constituent i/total mass
ω	Molecular weight	g/mole
ρ	Density of LNAPL constituent	g/cm^3
ρ_N	Density of LNAPL	g/cm^3
Superscripts:		
0	initial value (time = 0)	
k	time step k	
Subscripts:		
i	constituent i	
N	LNAPL	
p	Pores	
r	Residual	
rel	Release	
vad	Vadose zone	

4.1 LNAPL Retained in the Vadose Zone

The volume of LNAPL retained in the vadose zone depends on the volume in which the LNAPL is presumed to be released and the assumed LNAPL residual saturation in the vadose zone. The volume of the vadose zone that incorporates LNAPL is calculated from the DTW and release area at the release location.

First, the volume of LNAPL released (V_{rel}) is converted from gallons (gal) to ft^3:

$$1) \qquad V_{rel} = 27{,}000[gal]\frac{0.13368[ft^3]}{[gal]} = 3{,}609[ft^3]$$

The total volume of vadose zone containing LNAPL is:

$$2) \qquad V_{vad} = DTW \times A_{rel} = 85[ft]500[ft^2] = 42{,}500[ft^3]$$

where DTW is depth to water and A_{rel} is the area of the release at the ground surface. The pore volume in the vadose zone is then:

$$3)\qquad V_{p,vad} = n_{vad}V_{vad} = 0.1171 \times 42{,}500[ft^3] = 4{,}975[ft_p^3]$$

where $V_{p,vad}$ is the affected pore volume in the vadose zone and n_{vad} is the vadose zone average porosity calculated for the release location. The volume of LNAPL retained in the vadose zone ($V_{N,vad}$) is the vadose zone pore volume multiplied by the vadose zone LNAPL residual saturation ($S_{Nr,vad}$):

$$4)\qquad V_{N,vad} = S_{Nr,vad}V_{p,vad} = 0.0182\,\frac{ft_N^3}{ft_p^3} \times 4{,}975[ft_p^3] = 91[ft_N^3]$$

In this example calculation, approximately 2.5 percent (%) of the 27,000 gallons of LNAPL released is retained in the vadose zone, and the remaining 97.5% reaches the water table to form an LNAPL lens.

4.2 LNAPL Lens Size on the Water Table

The size of the LNAPL lens depends on the assumed LNAPL thickness and the average LNAPL lens saturation at the water table. First, the volume of LNAPL reaching the water table ($V_{N,sat}$) is calculated from the total release volume and the volume retained in the vadose zone:

$$5)\qquad V_{N,sat} = V_{rel} - V_{N,vad} = 3{,}609[ft^3] - 91[ft^3] = 3{,}509[ft^3]$$

The LNAPL volumetric content in saturated zone LNAPL lens ($\theta_{N,sat}$) is the LNAPL saturation multiplied by the specified saturated zone porosity, n_{sat}:

$$6)\qquad \theta_{N,sat} = S_{N,sat}n_{sat} = 0.4 \times 0.117 = 0.0468\left[\frac{ft_N^3}{ft^3}\right]$$

The LNAPL lens area is calculated from the specified LNAPL lens thickness (b_{lens}), the volume of LNAPL in the lens, and the calculated LNAPL volumetric content:

$$7)\qquad A_{lens} = \frac{V_{N,sat}}{b_{lens}\theta_{N,sat}} = \frac{3{,}509[ft_N^3]}{3[ft]0.0468\frac{ft_N^3}{ft^3}} = 25{,}000[ft^2]$$

If the LNAPL lens is assumed to be circular, then the radius of the LNAPL lens (r_{lens}) is calculated from the LNAPL lens area:

$$8)\qquad r_{lens} = \sqrt{\frac{A_{lens}}{\pi}} = \sqrt{\frac{25{,}000[ft^2]}{\pi}} = 89[ft]$$

4.3 Partitioning of LNAPL Constituents into Groundwater

The partitioning module of the VZM calculates the concentrations of LNAPL constituents within the LNAPL lens over time. 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 within the LNAPL lens are equal to the effective solubility of the LNAPL constituents. Effective solubility is the solubility of a pure phase component multiplied by its mole fraction in the LNAPL. Input parameters for the partitioning module are obtained from the other tabs in the heuristic model.

4.3.1 Initial Calculations

The partitioning module first calculates the Darcy flux (specific discharge, q) through the LNAPL area using the specified groundwater gradient (i). water relative permeability (k_{rel}), and hydraulic conductivity (K):

9) $$q = Kk_{rel}i$$

If the "Account for relative permeability" flag is equal to 1 on the Main tab, then the k_{rel} is set equal to the square of the water saturation ($1\text{-}S_{N,sat}$), analogous to the expression for a simplified LNAPL relative permeability suggested by Charbeneau and Chiang (1995). The volume of water flowing through the LNAPL lens is then calculated by multiplying the specific discharge by the cross-sectional area of the LNAPL lens:

10) $$Q = qwb$$

where w is the LNAPL lens width (assumed equal to the square root of the LNAPL area under the assumption of a square LNAPL lens shape) and b is the specified LNAPL lens thickness. The concentration of each constituent in the groundwater depends on the mole fraction of the constituent in the LNAPL. The mole fraction of each constituent is calculated by dividing the moles of each constituent (N_i^0) by the total moles initially present in the LNAPL (N_T^0):

11) $$x_i^0 = \frac{N_i^0}{N_T^0}$$

The initial effective solubility of the constituent (Se_i^0) is calculated from the mole fraction and pure phase solubility of the constituent, S_i :

12) $$Se_i^0 = x_i^0 S_i$$

The initial LNAPL density is calculated from the density of each LNAPL constituent:

13) $$\rho_N = \sum_{i=1}^{n} x_i \rho_i$$

4.3.2 Sequential Time Step Calculations

The concentrations of each LNAPL constituent in the groundwater are calculated at each time step based on the current composition of the LNAPL. As water flows through the LNAPL, the water dissolves a fraction of each soluble LNAPL constituent. To account for differential dissolution of the soluble LNAPL component in the model, the composition of the LNAPL is updated at each time step, and the total remaining volume of LNAPL is calculated. In these sequential time step calculations, new values are indicated with a "k+1" superscript, and old values are indicated with a "k" superscript.

First, the number of moles of each constituent (N_i^{k+1}) in the LNAPL lens following loss of the mass dissolved in groundwater is calculated for each time step:

14) $$N_i^{k+1} = N_i^k - \frac{QSe_i^k}{\omega_i}\Delta t$$

where Q is the volumetric flow rate through the LNAPL, ω_i is the molecular weight of the constituent, and Δt is the length of the partitioning module time step. The total number of moles of all constituents remaining in the LNAPL, N_T^{k+1}, is the sum of the moles of each constituent:

15) $$N_T^{k+1} = \sum_{i=1}^{n} N_i^{k+1}$$

The new mole fraction of each constituent (x_i^{k+1}) is then calculated, and the new effective solubility of each constituent (Se_i^{k+1}) is calculated based on the mole fraction and pure phase solubility:

16) $$x_i^{k+1} = \frac{N_i^{k+1}}{N_T^{k+1}}$$

17) $$Se_i^{k+1} = x_i^{k+1} S_i f_{sweep}$$

The f_{sweep} parameter accounts for only partial contact of the groundwater with LNAPL, and is set equal to the LNAPL lens saturation if the "Account for sweep efficiency" flag is set to 1 on the Main tab. Finally, the volume of LNAPL remaining after the loss of each constituent by dissolution in groundwater is calculated based on the molar volumes of each constituent:

18) $$V_N^{k+1} = \sum_{i=1}^{n} \frac{(N_i^{k+1} - N_i^k)\omega_i}{\rho_i}$$

The sequential calculations shown in Equations 14 through 18 above are repeated for each time step to determine the concentration of each constituent in groundwater and the volume of LNAPL remaining over the time desired.

4.3.3 Partition Module Calculation Verification

The calculated dissolved phase concentration histories of the VZM partitioning module were compared to the dissolved phase concentration history calculations of the model published by the 2005 American Geophysical Union (AGU) publication "Soil and Groundwater Contamination: Nonaqueous Phase Liquids, AGU Water Resources Monograph 17" (Mayer and Hassanizadeh 2005). As shown in Figure 7, the partitioning module of the VZM reproduces the results of the AGU model for the same example set of LNAPL constituents that represent a wide range of chemical properties, indicating that the partitioning model calculations are performed correctly in the VZM spreadsheet.

5.0 Results

The LNAPL lens size and groundwater concentrations calculated with the VZM for the three historical and twelve hypothetical scenarios evaluated are provided in Table 1. With the conservative parameters specified for these model runs, very little LNAPL is retained in the vadose zone and dissolved concentrations diminish very slowly. The maximum lens radius of 1400 ft calculated for the large release is a strong function of the relatively large assumed LNAPL lens thickness of 5 ft and the relatively high expected LNAPL lens saturation of 0.5.

In general, the LNAPL lens area and computed lens radius increase with the release size regardless of the release location. For all small release sizes, the computed LNAPL lens radius is approximately 80 to 90 feet. The LNAPL lens radii ranges for the medium and large releases are approximately 180 to 210 and 1,300 to 1,400 feet, respectively. The TPH-d concentrations also increase with release size, which reflects the increase in assumed LNAPL saturation with increasing LNAPL lens thickness. Because the fraction of LNAPL retained in the vadose zone is small for all release scenarios except for the actual November 2021 release, the depth to water has only a minor effect on the LNAPL lens size.

The area of the LNAPL lens, the TPH-d concentrations in the LNAPL lens, and the LNAPL lens constituent concentrations are used to establish boundary conditions for the CF&T model.

6.0 Model Limitations

This VZM was developed for the sole purpose of conservatively estimating a source term for the dissolved groundwater CF&T modeling. The model does not account for the unknown and highly heterogenous subsurface architecture. As a result, the VZM does not depict travel paths and rates through the vadose zone. Rather, the VZM model conservatively estimates the amount of LNAPL released at the surface that is retained in the vadose zone and the amount that reaches and spreads on the water table. This conceptual model of instantaneous distribution between the vadose zone and saturated zone is consistent with the rapid downward migration and small horizontal deflection observed after the November 2021 release.

Because of the extreme complexity of subsurface volcanic environments, many parameters for even the simple VZM described herein are highly uncertain. Specifically, the VZM does not account for:

- strike and dip of rock formations;
- hydraulic conductivity heterogeneity;
- different rates of migration through different types of rock;
- preferential flow pathways created by lava tubes, clinker layers, fractures, and other preferential subsurface heterogeneities;
- flow of water and dissolved LNAPL constituents in the vadose zone;
- long-term changes in drainage of LNAPL from the vadose zone;
- lateral movement of LNAPL in the vadose zone;
- variable residual LNAPL saturation in the vadose zone;

- variable LNAPL thickness and saturations within the LNAPL lens that forms on the water table;
- capillary retention in the vadose zone and saturated zone;
- variable LNAPL residual saturations caused by imbibement of LNAPL under variable LNAPL head;
- changes in LNAPL physical properties caused by weathering and dissolution of soluble constituents;
- actual shape of the LNAPL lens on the water table;
- transient changes in the groundwater hydraulic gradient;
- specific types of fuel and fuel compositions of potential undocumented historical releases.

These substantial limitations should be kept in mind when interpreting the results of the VZM.

7.0 Next Steps

The Navy requested that an expedited set of models and modeling memoranda including groundwater flow, vadose zone, and CF&T models be completed by June 30, 2023. An expedited modeling path that includes the VZM described herein provides the Navy with a set of tools for decision making in the near-term. After June 30, 2023, the next formal deliverable will be a final modeling document to be delivered to the Navy in September 2024.

The next step in the VZM that will be included in the September 2024 deliverable is the incorporation of additional model details added as feasible, and as necessary to respond to stakeholder concerns. These will be designed to lead to a better representation of the subsurface. Because substantial uncertainty in the subsurface architecture will remain, inclusion of additional detail and processes will still not provide a single outcome for a given release, but rather a range of possible outcomes that can be used to plan for a reasonable worst-case scenario of LNAPL migration following a particular release.

8.0 References

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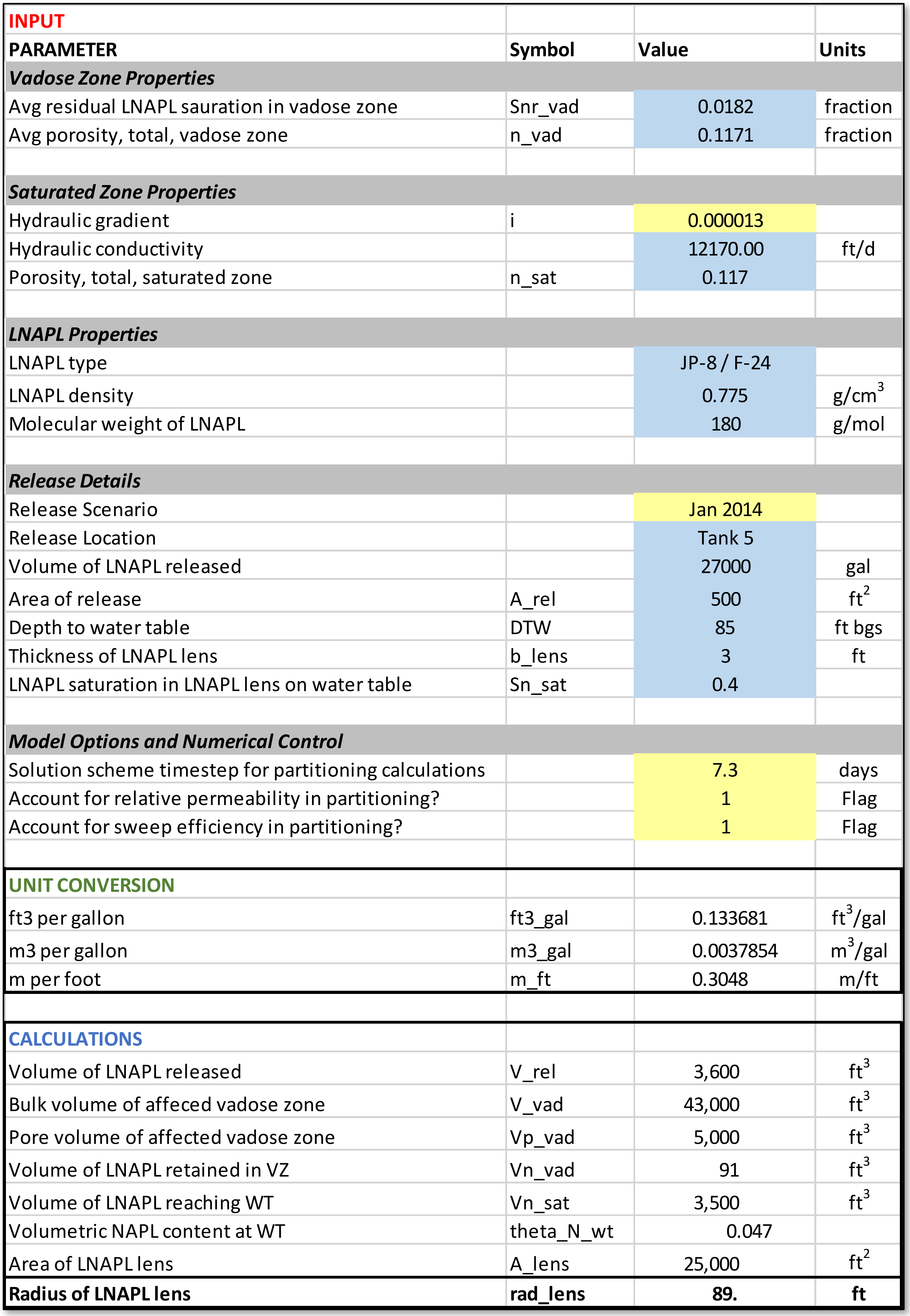
Table 1
Simulated Release Scenarios and Heuristic Model Results

INPUTS					OUTPUTS						
Release Scenario Size	Release Location	Volume of LNAPL released (gal)	Average LNAPL Thickness in Lens (ft)	Average LNAPL Saturation in LNAPL Lens	Volume of LNAPL Retained in VZ[1] (gal)	Volume of LNAPL Reaching WT[2] (gal)	Volumetric NAPL Content at WT[3]	Area of LNAPL Lens (ft^2)	Radius of LNAPL Lens (ft)	TPH-d Conc. in LNAPL Lens[4] (mg/L)	TPH-d Conc. in 25-ft Model Grid Cell[5] (mg/L)
Small	Tank 5	12,500	2	0.3	680	11,820	0.035	22,000	85	1.69	0.14
Small	Tanks 18 and 20	12,500	2	0.3	620	11,880	0.031	26,000	90	1.69	0.14
Small	RHMW05	12,500	2	0.3	760	11,740	0.038	21,000	81	1.69	0.14
Small	RHS / Adit 3	12,500	2	0.3	830	11,670	0.039	20,000	79	1.69	0.14
Medium	Tank 5	125,000	3	0.4	680	124,320	0.047	120,000	190	2.25	0.27
Medium	Tanks 18 and 20	125,000	3	0.4	620	124,380	0.041	130,000	210	2.25	0.27
Medium	RHMW05	125,000	3	0.4	760	124,240	0.051	110,000	190	2.25	0.27
Medium	RHS / Adit 3	125,000	3	0.4	830	124,170	0.053	110,000	180	2.25	0.27
Large	Tank 5	12,500,000	5	0.5	680	12,499,320	0.059	5,700,000	1,300	2.82	0.56
Large	Tanks 18 and 20	12,500,000	5	0.5	620	12,499,380	0.052	6,500,000	1,400	2.82	0.56
Large	RHMW05	12,500,000	5	0.5	760	12,499,240	0.063	5,300,000	1,300	2.82	0.56
Large	RHS / Adit 3	12,500,000	5	0.5	830	12,499,170	0.066	5,100,000	1,300	2.82	0.56
Jan 2014	Tank 5	27,000	3	0.4	680	26,320	0.047	25,000	89	2.55	0.31
May 2021	Tanks 18 and 20	100	0.2	0.05	100	0	0.0052	0	0	NA	NA
Nov 2021	RHS / Adit 3	5,000	1	0.2	830	4,170	0.026	21,000	82	1.13	0.045

Notes:

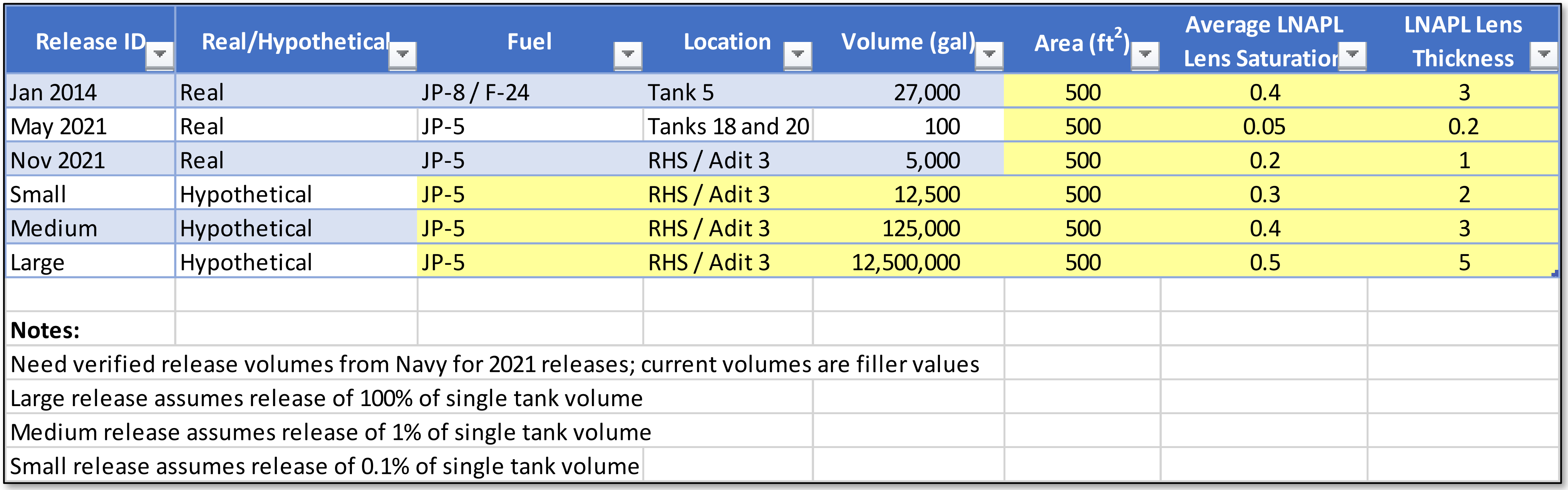
1. VZ = vadose zone.
2. WT = water table.
3. Volumetric LNAPL content at WT = the volume of LNAPL per unit total bulk volume within the LNAPL lens in the saturated zone.
4. TPH-d Conc. in LNAPL lens = the dissolved phase TPH-d concentration in groundwater within the LNAPL zone.
5. TPH-d Conc. in 25-ft Model Grid Cell = The groundwater concentration within the LNAPL lens, adjusted for the fact that the LNAPL lens thickness is smaller than the thickness of the 25-ft thick CFT model cell. The LNAPL lens concentrations are multiplied by the ratio of LNAPL lens thickness to CFT model grid thickness to account for this dilution of the boundary condition concentration.

Figure 1
Main Tab of the Heuristic Model



INPUT			
PARAMETER	**Symbol**	**Value**	**Units**
Vadose Zone Properties			
Avg residual LNAPL sauration in vadose zone	Snr_vad	0.0182	fraction
Avg porosity, total, vadose zone	n_vad	0.1171	fraction
Saturated Zone Properties			
Hydraulic gradient	i	0.000013	
Hydraulic conductivity		12170.00	ft/d
Porosity, total, saturated zone	n_sat	0.117	
LNAPL Properties			
LNAPL type		JP-8 / F-24	
LNAPL density		0.775	g/cm^3
Molecular weight of LNAPL		180	g/mol
Release Details			
Release Scenario		Jan 2014	
Release Location		Tank 5	
Volume of LNAPL released		27000	gal
Area of release	A_rel	500	ft^2
Depth to water table	DTW	85	ft bgs
Thickness of LNAPL lens	b_lens	3	ft
LNAPL saturation in LNAPL lens on water table	Sn_sat	0.4	
Model Options and Numerical Control			
Solution scheme timestep for partitioning calculations		7.3	days
Account for relative permeability in partitioning?		1	Flag
Account for sweep efficiency in partitioning?		1	Flag
UNIT CONVERSION			
ft3 per gallon	ft3_gal	0.133681	ft^3/gal
m3 per gallon	m3_gal	0.0037854	m^3/gal
m per foot	m_ft	0.3048	m/ft
CALCULATIONS			
Volume of LNAPL released	V_rel	3,600	ft^3
Bulk volume of affeced vadose zone	V_vad	43,000	ft^3
Pore volume of affected vadose zone	Vp_vad	5,000	ft^3
Volume of LNAPL retained in VZ	Vn_vad	91	ft^3
Volume of LNAPL reaching WT	Vn_sat	3,500	ft^3
Volumetric NAPL content at WT	theta_N_wt	0.047	
Area of LNAPL lens	A_lens	25,000	ft^2
Radius of LNAPL lens	**rad_lens**	**89.**	**ft**

Figure 2
Release Info Tab of the Heuristic Model



Release ID	Real/Hypothetical	Fuel	Location	Volume (gal)	Area (ft^2)	Average LNAPL Lens Saturation	LNAPL Lens Thickness
Jan 2014	Real	JP-8 / F-24	Tank 5	27,000	500	0.4	3
May 2021	Real	JP-5	Tanks 18 and 20	100	500	0.05	0.2
Nov 2021	Real	JP-5	RHS / Adit 3	5,000	500	0.2	1
Small	Hypothetical	JP-5	RHS / Adit 3	12,500	500	0.3	2
Medium	Hypothetical	JP-5	RHS / Adit 3	125,000	500	0.4	3
Large	Hypothetical	JP-5	RHS / Adit 3	12,500,000	500	0.5	5

Notes:

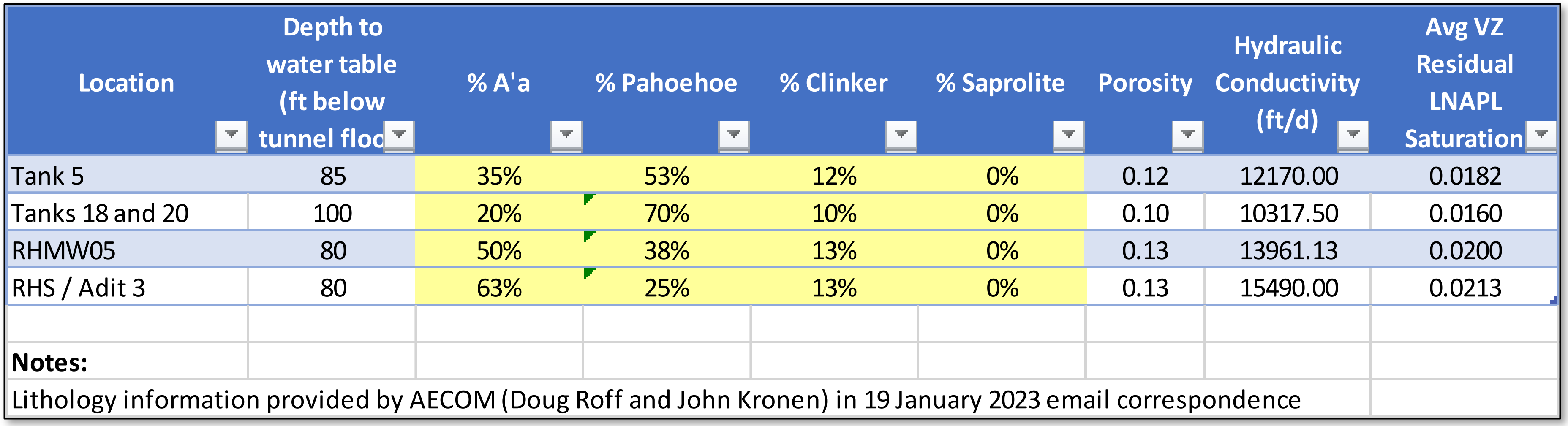
Need verified release volumes from Navy for 2021 releases; current volumes are filler values

Large release assumes release of 100% of single tank volume

Medium release assumes release of 1% of single tank volume

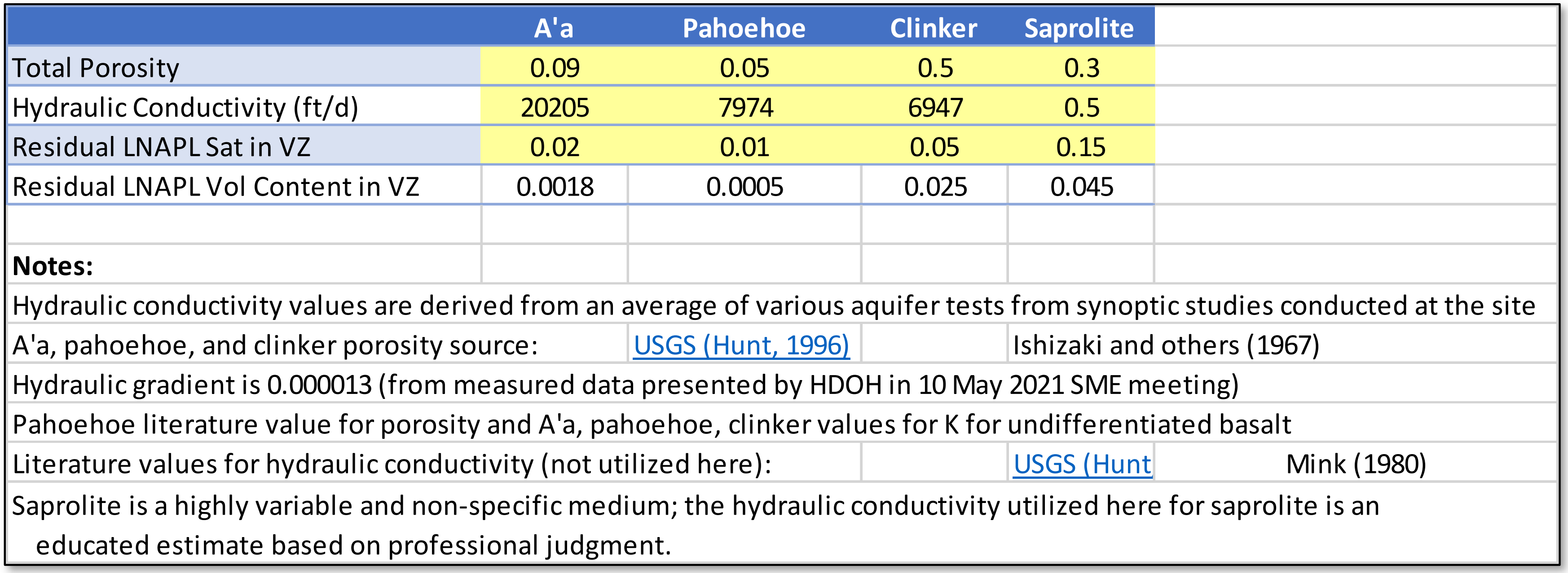
Small release assumes release of 0.1% of single tank volume

Figure 3
Location Info Tab of the Heuristic Model



Location	Depth to water table (ft below tunnel floo	% A'a	% Pahoehoe	% Clinker	% Saprolite	Porosity	Hydraulic Conductivity (ft/d)	Avg VZ Residual LNAPL Saturation
Tank 5	85	35%	53%	12%	0%	0.12	12170.00	0.0182
Tanks 18 and 20	100	20%	70%	10%	0%	0.10	10317.50	0.0160
RHMW05	80	50%	38%	13%	0%	0.13	13961.13	0.0200
RHS / Adit 3	80	63%	25%	13%	0%	0.13	15490.00	0.0213
Notes:								
Lithology information provided by AECOM (Doug Roff and John Kronen) in 19 January 2023 email correspondence								

Figure 4
Hydrogeologic Info Tab of the Heuristic Model



	A'a	Pahoehoe	Clinker	Saprolite
Total Porosity	0.09	0.05	0.5	0.3
Hydraulic Conductivity (ft/d)	20205	7974	6947	0.5
Residual LNAPL Sat in VZ	0.02	0.01	0.05	0.15
Residual LNAPL Vol Content in VZ	0.0018	0.0005	0.025	0.045

Notes:

Hydraulic conductivity values are derived from an average of various aquifer tests from synoptic studies conducted at the site

A'a, pahoehoe, and clinker porosity source: USGS (Hunt, 1996) Ishizaki and others (1967)

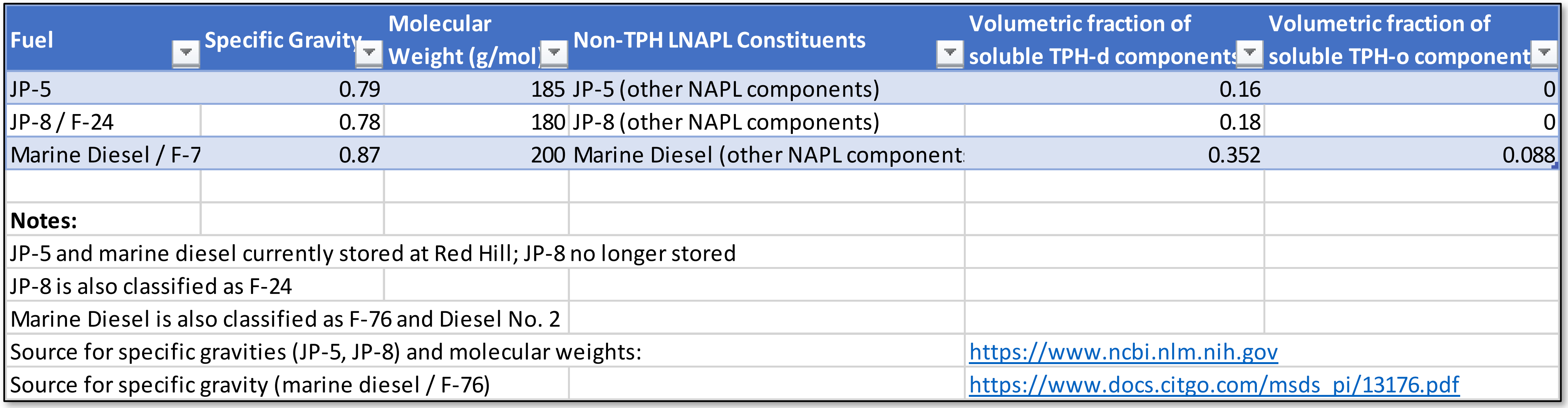
Hydraulic gradient is 0.000013 (from measured data presented by HDOH in 10 May 2021 SME meeting)

Pahoehoe literature value for porosity and A'a, pahoehoe, clinker values for K for undifferentiated basalt

Literature values for hydraulic conductivity (not utilized here): USGS (Hunt Mink (1980)

Saprolite is a highly variable and non-specific medium; the hydraulic conductivity utilized here for saprolite is an educated estimate based on professional judgment.

Figure 5
Fuel Info Tab of the Heuristic Model



Fuel	Specific Gravity	Molecular Weight (g/mol	Non-TPH LNAPL Constituents	Volumetric fraction of soluble TPH-d component	Volumetric fraction of soluble TPH-o component
JP-5	0.79	185	JP-5 (other NAPL components)	0.16	0
JP-8 / F-24	0.78	180	JP-8 (other NAPL components)	0.18	0
Marine Diesel / F-7	0.87	200	Marine Diesel (other NAPL component	0.352	0.088
Notes:					
JP-5 and marine diesel currently stored at Red Hill; JP-8 no longer stored					
JP-8 is also classified as F-24					
Marine Diesel is also classified as F-76 and Diesel No. 2					
Source for specific gravities (JP-5, JP-8) and molecular weights:				https://www.ncbi.nlm.nih.gov	
Source for specific gravity (marine diesel / F-76)				https://www.docs.citgo.com/msds_pi/13176.pdf	

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Issued: 26 April 2023

Figure 6
Partitioning Tab of the Heuristic Model

INPUT CELLS / TABS
FROM HEURISTIC MODEL
LOOKUP CELLS

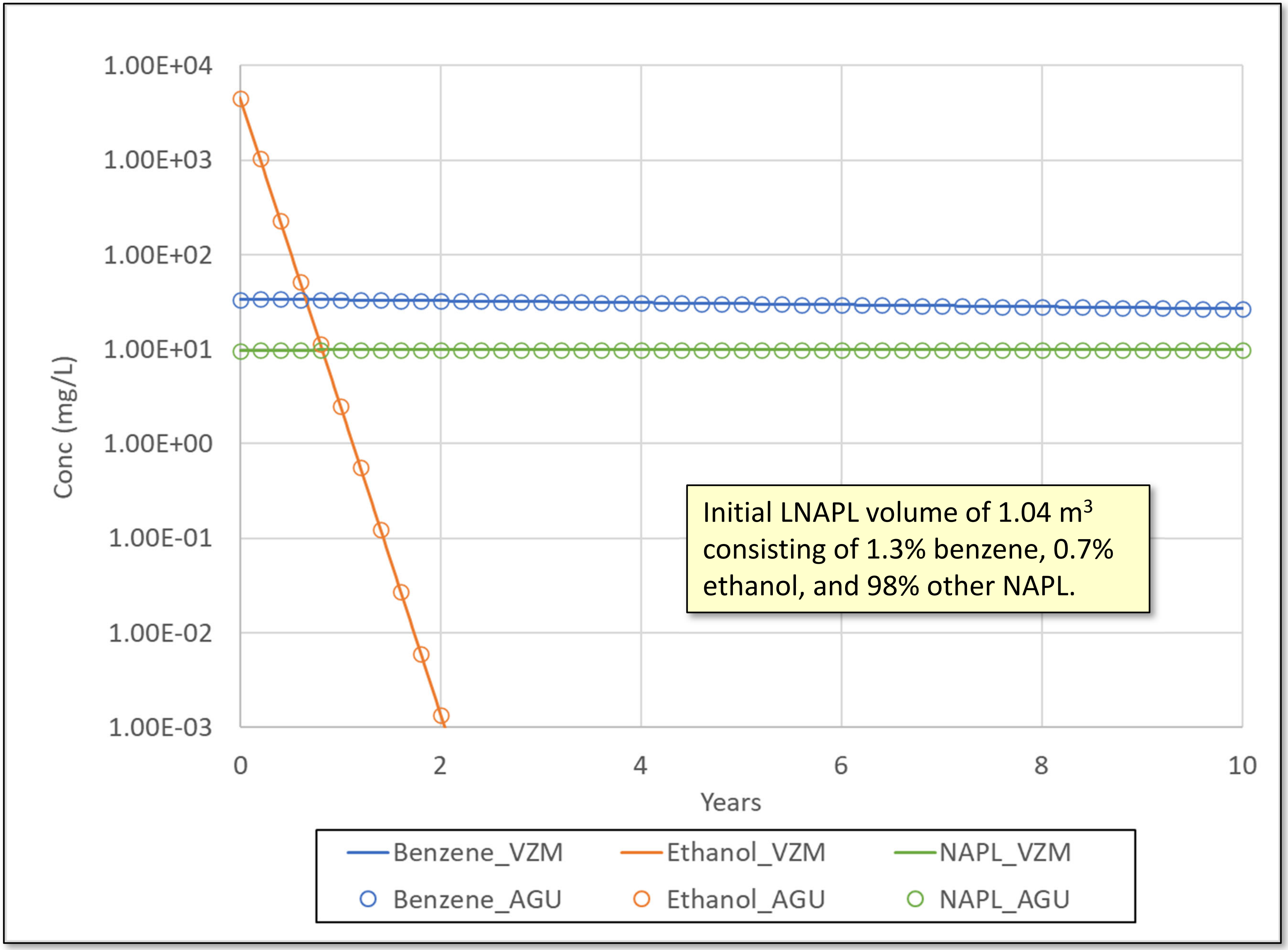
Parameter	Symbol	Value	Units	Comments
General Parameters:				
Hydraulic conductivity	K_sat	4721.352	m/d	Unit conversion.
Hydraulic gradient	i	0.000013		
Width of LNAPL lens	w	217	m	Assume a square shape.
Average thickness of LNAPL lens	b	1.52	m	Unit conversion.
Length of LNAPL lens	L	217	m	Assume a square shape.
Solution scheme time step	dt	7	d	
LNAPL volume in lens	V_N	4728.621363	m^3	Unit conversion.
Porosity of saturated zone	por	0.13	fraction	
Account for relative permeability?	RFLAG	1		1 = Yes, 0 = No. Multipies Q_gw by k_rel in calc of mols.
Account for sweep eff?	SWPFLAG	1		1 = Yes, 0 = No. Multiplies Se by Sn in calculation of Conc.

LNAPL Constituent Parameters and Initial Values:

Constituent	MW g/mol	Solubility (mg/L)	Vol Fract yi	Vol (m^3)	Density (g/cm^3)	Initial mols	Initial Mol Fract	Initial Mass Fract	Initial Mass (kg)	Difference Mass/Vol Fract
TPH-d soluble components (C10-C24)	130	25	0.16	756.579418	0.780	4.54E+06	0.225	0.158	5.90E+05	1%
TPH-o soluble components (C24-C40)	240	0.0066	0	0	0.870	0.00E+00	0.000	0.000	0.00E+00	NA
JP-5 (other NAPL components)	201.04	0	0.84	3972.04195	0.790	1.56E+07	0.775	0.842	3.14E+06	0%
			1.000	4728.62136		2.01E+07	1.000	1.000	3.73E+06	

Parameter	Symbol	Value	Units	Comments	
Calculated Quantities:					
Specific discharge	q	6.14E-02	m/d		
Seepage velocity	v	4.68E-01	m/d	5.60E+02	ft/yr
LNAPL lens cross-sectional area	Ax_lens	3.31E+02	m^2		
Volumetric flow rate through LNAPL	Q_gw	2.03E+01	m^3/d		
Average LNAPL molecular weight	MW_LNAPL	1.85E+02	g/mol		
Total initial moles	N_T^0	2.01E+07	mol		
LNAPL density	den_N	7.88E-01	g/cm^3		
Initial LNAPL mass	M_N	3.73E+06	kg		
Release media volume	V_T	7.21E+04	m^3		
Release media pore volume	V_P	9.46E+03	m^3		
Initial LNAPL saturation	S_Ni	5.00E-01	fraction		
Initial LNAPL content	theta_N	6.56E-02	fraction		
Initial water content	theta_w	6.56E-02	fraction	-	
Initial water relative permeability	k_rel	2.50E-01	fraction		

Figure 7
VZM Partitioning Module Output Compared to the AGU Model of Mayer and Hassanizadeh (2005)



Initial LNAPL volume of 1.04 m^3 consisting of 1.3% benzene, 0.7% ethanol, and 98% other NAPL.