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Calculation Cover Sheet

Project Method to Determine and Quantify Non-Aqueous Phase Liquids in Environmental Media		Calculation Number Q-CLC-G-00059, Rev. 0	Project Number NA
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Purpose and Objective The purpose of this calculation is to document the method and equations for the determination and quantification of non-aqueous phase liquids in environmental media.			
Summary of Conclusion – The calculations were successfully performed by the software for three case scenarios. The case scenarios were computed with the software and the calculations were hand checked to verify the results.			
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1.0 INTRODUCTION

Non-aqueous phase liquid, or “NAPL,” is a term that most environmental professionals are familiar with because it has been recognized in the literature as a significant source of groundwater contamination. There are two types of NAPL: DNAPL and LNAPL. DNAPL is a “dense” non-aqueous phase liquid. In this context, the term “dense” refers to density greater than 1.0 kg/L. Trichloroethylene (TCE) and tetrachloroethylene (PCE) are common examples of DNAPL compounds (Reference Figure 1). A DNAPL compound that is heavier than water will sink in an aquifer. Conversely, LNAPL is a “light” non-aqueous phase liquid with a density less than 1.0 kg/L and will float on top of the aquifer. Examples of LNAPLs include benzene and toluene. Both LNAPL and DNAPL often manifest as complex, multi-component mixtures of organic compounds that can occur in environmental media other than groundwater, such as vadose zone soil, in which a contaminant will partition and contaminate soil particles, soil pore air, and soil pore water. Complex multi-component mixtures distributed in soil pore air, soil pore water, and soil particles complicate identification of NAPL in the various phases of soil media.

The discovery of NAPL in the aquifer under a waste site usually leads to a focused characterization for possible sources of NAPL in the vadose zone using a variety of conventional and innovative technology characterization methods. Often the soil or soil vapor analytical data will indicate the presence of a NAPL, yet the NAPL may be overlooked by site investigators. Possible reasons NAPL may be overlooked is because it can occur as a thin, discrete layer or because the concentration indicating a NAPL may occur at a much lower threshold than anticipated. The failure to recognize the presence of NAPL can be attributed to the complicated processes of inter-media transfer in the soil media and the fact that chemical properties do change in complex organic mixtures in environmental samples. Identification of NAPL in various phases of soil media is complicated by changes in the physical and chemical properties of the organic compounds present in these mixtures.



(Note: This is a worst-case example of extraction of free product from an aquifer well indicating mobile DNAPL from a vadose zone source. This sample consists of tetrachloroethylene, polychlorinated biphenol, and trichloroethylene in order of mass composition).

Figure 1. Dense Non-Aqueous Phase Liquid from a Groundwater Monitoring Well at the Savannah River Site

The most important property change is solubility although other important properties such as vapor pressure and density also change. In the case of a NAPL that behaves as an ideal mixture, the solubility of the mixture will always be less than the greater of its pure phase components. Not only does this make the identification of the NAPL more difficult, but the NAPL threshold may occur at a much lower threshold than is assumed.

Relative low solubility is one of the reasons NAPL is persistent in the environment. Low solubility is also the reason some conventional remedial technologies fail to perform or perform poorly at some waste sites. For these reasons, the presence of NAPL at waste sites may be vastly under reported or underestimated. The recognition and quantification of NAPL in the primary or secondary source at a waste site is essential in order to design and operate an effective remedial system. Remedial measures that have been implemented where the presence of NAPL has been overlooked have resulted in longer than expected clean-up times and rebounding effects after remedies have been implemented because residual NAPL remains trapped in the soil and acts as a continuing source of contamination to the groundwater. In many of these instances, removal of the NAPL is rate limited because of the time required for diffusion in vapor or liquid phase from pore spaces in clayey and silty soils.

1.1 NAPL Analytical Models

A search of relevant literature reveals that there may be only one “stand alone” analytical modeling solution to calculate NAPL saturation and volume for complex organic mixtures in a soil sample. This model is called NAPLANAL (Mariner et al. 1997). NAPLANAL is a stand-alone model and estimates NAPL saturation, including media concentrations and masses, as well as estimations of the volume occupied by NAPL. The analytical method for NAPLANAL uses a system of equations and constraints to solve for unknowns by an iteration process. The iterations are bounded by pre-defined governing equations. While the calculated statistical residual for the NAPLANAL model is usually very small (less

than 1.0×10^{-6}), the solution is not exact and there is some question of the model's accuracy when contaminant masses are low (100 mg/kg or less) using this model.

A second model NAPL Calculator (NAPLator) has been developed and is the subject of this calculation note. Its operation builds upon the NAPLANAL model, but it uses a different method of calculation and estimates additional metrics. NAPLator uses modified algorithms of the NAPLANAL to converge at an exact analytical solution. There are no statistical residuals, not even minor ones. The NAPLator model uses a classic chemistry approach to sequentially solve a series of equations to compute the molar fraction, effective solubility, density, effective vapor pressure, soil saturation limit, NAPL mass, NAPL volume, and residual saturation.

Information outputs of the NAPLator include the soil saturation limit, volumetric soil saturation limit, concentrations contained in each media, masses within each media, total NAPL mass, NAPL volume within the soil voids, NAPL density, percent composition of the NAPL, total mass of each contaminant, effective solubility, total solubility of mixtures, effective vapor pressure, total vapor pressure of the mixture, and built-in graphing capability to illustrate NAPL physical and chemical properties. Additionally, there is an extended database of chemical properties. The model will estimate concentrations for either saturated or unsaturated media samples while conserving all mass and volume.

Table 1 compares the features of both NAPLANAL and NAPLator.

Table 1. Comparison of Two NAPL Models

Feature	NAPLANAL	NAPLator
Operating Platform	Stand alone	MS Excel•©
Calculates NAPL Saturation	Yes	Yes
Calculates NAPL Volume	Yes	Yes
Calculates Total NAPL Mass	No, by compound only	Yes, by compound and total
Calculates NAPL Density	Yes	Yes
Calculates Media Masses	Yes	Yes
Calculates Media Concentrations	Yes	Yes
Calculates Media Volumes	Yes	Yes
Built-in Data Base of Chemical Properties	Yes	Yes, but more extensive
Outputs Soil Saturation Limit	No	Yes
Outputs Effective Solubility	No	Yes
Calculates Effective Vapor Pressure	No	Yes
Calculates Mixture Properties	No	Yes
Calculates Volumetric Air Concentration	No	Yes
Provides Graphic Output	No	Yes
Numerical Accuracy	Almost exact with errors at low concentrations	Exact
Mass Balance for each Compound	No	Yes
Volumetric Balance Displayed Output	Yes	Yes

Table 2a lists the input parameters for the comparison examples shown in Table 2b and Table 3. These tables show examples that compare the accuracy and type of results derived from both models. In both examples, all the input parameters are kept the same with the exception of the contaminant masses and chemical-specific properties.

Table 2a. Geologic/Chemical Specific Input Properties for Two Comparison Examples

Input Parameter	Tetrachloroethylene (PCE)	Trichloroethylene (TCE)
Molecular Weight (g/mol)	165.85	131.29
Aqueous Solubility (mg/L)	200.0	1100.0
Vapor Pressure (mmHg)	18.47	74.31
Henry's Law Constant (unitless)	0.943	0.3649
Carbon Partitioning Coefficient (L/kg)	364.0	126.0
Density (kg/L)	1.63	1.46
Fraction Organic Carbon (%)	0.0001	.0001
Total Porosity (%)	40	40
Moisture Content (%)	20	20
Contaminant Mass Example 1 (mg/kg)	100.0	100.0
Contaminant Mass Example 2 (mg/kg)	400.0	900.0

Table 2b. Example 1 - Comparison of NAPLANAL and NAPLator Model Results

Parameter	NAPLANAL		NAPLator	
	PCE	TCE	PCE	TCE
Soil Saturation Limit (mg/kg)	Not Calculated	Not Calculated	22.39	101.34
NAPL Saturation (%)	0.0288		0.0226	
NAPL Mass (mg/kg)	68.60	32.45	77.60	0.0
NAPL Present in Sample	Yes	Yes	Yes	No
Mole Fraction (%)	0.6260	0.3740	0.4418	0.5582
Effective Solubility (mg/L)	Not Calculated	Not Calculated	88.37	613.97
Effective Vapor Pressure (mmHg)	Not Calculated	Not Calculated	8.16	41.48
NAPL Density (kg/L)	1.57		1.54	
NAPL Volume (fraction)	0.000115		0.00009	
Air Volume (fraction)	0.1999		0.1999	
Bulk Density (kg/L)	1.79		1.79	
Volumetric Air Concentration (ppmv@20C)	Not Calculated	Not Calculated	12,086.67	40,502.99
Solubility of Mixture (mg/L)	Not Calculated		702.34	
Vapor Pressure of Mixture (mmHg)	Not Calculated		49.64	
Pore Water Concentration (mg/L)	125.2	411.41	88.37	605.81

Table 3. Example 2 - Comparison of NAPLANAL and NAPLator Results

Parameter	NAPLANAL		NAPLator	
	PCE	TCE	PCE	TCE
Soil Saturation Limit (mg/kg)	Not Displayed	Not Displayed	13.18	134.19
NAPL Saturation (%)	0.3427		0.3433	
NAPL Mass (mg/kg)	385.82	770.97	386.82	765.82
NAPL Present in Sample	Yes	Yes	Yes	Yes
Mole Fraction (%)	0.2837	0.7163	0.2603	0.7397
Effective Solubility (mg/L)	Not Calculated	Not Calculated	52.05	813.71
Effective Vapor Pressure (mmHg)	Not Calculated	Not Calculated	4.81	54.97
NAPL Density (kg/L)	1.51		1.50	
NAPL Volume (fraction)	0.00137		0.00137	
Air Volume (fraction)	0.19863		0.19863	
Bulk Density (kg/L)	1.79		1.79	
Volumetric Air Concentration (ppmv@20C)	Not Calculated	Not Calculated	7119.47	54,402.96
Solubility of Mixture (mg/L)	Not Calculated		865.76	
Vapor Pressure of Mixture (mmHg)	Not Calculated		59.78	
Pore Water Concentration (mg/L)	56.75	787.88	52.05	813.71

Table 2b indicates the occurrence of an inaccuracy in the NAPLANAL model algorithms at soil concentrations less than or equal to the 100 mg/kg. NAPLANAL overestimates NAPL mass in the sample because the mole fractions deviate from those calculated by the NAPLator model by approximately 20%. NAPLANAL reports a TCE NAPL mass when none actually occurs. NAPL mass does not exist for TCE because the soil saturation level does not exceed the total mass of TCE in the sample. Analysis of the reason for the NAPLANAL overestimation cannot occur because sufficient documentation of the algorithm routine does not exist for the NAPLANAL program to facilitate further evaluation. However, the inaccurate results reported by the NAPLANAL model would lead investigators to conclude a TCE/PCE NAPL mixture was present at this waste site

when, in fact, only a PCE NAPL was present in the sample. As concentration in the sample increase, deviations decrease.

In the second example, NAPL saturation, NAPL mass, and NAPL volume are almost identical and the differences are probably statistically insignificant. However, NAPLANAL still slightly overestimates mole fractions by 1 to 3% and is responsible for the minor deviations in the calculated values. These inconsistencies may be due to the differences in computational methods used in the models; however, sufficient documentation does not exist for the NAPLANAL model to permit evaluation. By contrast, NAPLator calculates exact solutions and reports metrics not reported in the NAPLANAL model. These additional metrics (soil saturation limit, effective solubility, effective vapor pressure, mixture solubility, mixture vapor pressure, volumetric vapor concentration, and mass balance for each compound) are important for characterization and understanding of the source for remedial activities. NAPLator provides a more useful and robust information output for which the analytical solutions are documented in this calc-note.

2.0 FOUNDATIONS FOR SOFTWARE CALCULATIONS

The calculations that are performed by the NAPLator model are based on a set of definitions that are derived from a number of scientific theories and laws. These are addressed in the following paragraphs as are the governing equations used to arrive at solutions and the operational steps of the software. The following fundamental assumptions apply to the calculations performed by the NAPLator model.

2.1 Assumptions

- The NAPL mixture will behave as an ideal solution. An ideal solution will obey Raoult's Law. The effects of co-solvency are not considered. Where large quantities of alcohol or acetone exist in a soil system NAPLator may not be a valid analytical model, but such is usually not the case.

- All mass and volume is conserved. There is no loss of mass or volume due to volatilization, degradation, evaporation, photolysis, etc. or other physical-chemical processes. At the end of the calculation, final mass and volume will equal the initial mass and volume.
- Contaminants are uniformly distributed throughout the contaminated media.
- Equilibrium partitioning is instantaneous and linear for vapor, aqueous, solid and NAPL phases.
- All NAPL or NAPL mixtures are liquids at ambient temperatures.
- Environmental media has three phases: soil particles, soil pore-air, and soil pore water.
- Mass is composed of four states: solid, vapor, aqueous, and NAPL.
- In a saturated sample, there is no air-filled porosity.
- Soil temperature is assumed to be a constant 20° C.

2.2 Solubility Limit Theory for NAPL

This most important definition states that if the concentration of an organic chemical mixed in water exceeds its pure-phase aqueous solubility limit, then NAPL is present in the sample. The most fundamental qualitative and quantitative test for NAPL is determined by comparing the solubility limit of an organic compound to its concentration in water. By application of equilibrium partitioning theory, theoretical upper bound, solubility-saturation related concentrations can be similarly calculated for other phases of media such as soil-vapor and sorbed-soil concentrations. In its simplest form, the definition for a NAPL can be expressed as:

NAPL exists where $C_{wi} > S_i$ or $C_{wi} > S_i^E$

Where:

C_{wi} = Water concentration

S_i = Aqueous-phase solubility limit of the organic compound i

S_i^E = Effective solubility limit of the organic compound i in a mixture

The following example illustrates the concept of this definition:

TCE was detected in a groundwater sample at a concentration of 2000.0 mg/L (C_w). A comparison of the groundwater analytical result (2000.0 mg/L) with that of the aqueous solubility limit for TCE (1100.0 mg/L) (S) indicated that NAPL was present in the groundwater sample because the concentration in the sample had exceeded the aqueous solubility limit for TCE, i.e., $C_w > S$. There was approximately 900 mg/L of TCE in free-phase (NAPL) in this sample.

This is the simplest example of how the solubility limit theory is used to determine the presence and mass of a NAPL in a groundwater sample. However, real world examples are seldom this straight forward. This example can become significantly more complicated if multiple organic compounds are in a mixture, and the compound has partitioned between soil particles, soil-pore air, and soil-pore water phases in the vadose zone. In practice, NAPL at a waste site is often detected as a mixture of organic compounds, not as a single organic compound, and in soil media, not in groundwater. Think about the following example:

The analysis of a vadose zone soil sample revealed 100.0 mg/kg of TCE and 100.0 mg/kg of PCE.

Is NAPL present in this soil sample? What compound(s) are NAPL and what mass of NAPL is present in this sample if there is NAPL? Is the soil concentration for each compound compared to its pure-phase solubility limit or does some other method need to be applied? What if there were three, four or more compounds in this mixture? The answer to some of the above questions requires the application of Raoult's Law.

2.3 Raoult's Law

Raoult's Law must first be used to answer some of the questions above by calculating what is termed the "effective solubility" (Feenstra et al.) for a multi-component organic compound. Raoult's Law states that the effective solubility of a compound is equal to the molar fraction of the compound in the mixture times its pure-phase solubility.

The law can be expressed mathematically as

$$S_i^E = X_i * S_i$$

Where:

S_i^E = Effective solubility of compound i in a mixture (mg/L)

X_i = Molar fraction of compound i in a mixture (% , unitless)

S_i = Pure phase solubility of the compound i (mg/L)

The molar fraction is determined by dividing the molar weight of compound i by the sum of molar weights of all the compounds in the mixture. Therefore, the sum of the molar fractions is equal to one. Assuming an ideal solution, Raoult's Law is applicable, and the resulting solubility of the mixture is equal to the sum of the effective solubilities. Like the solubility, density and vapor pressure for a mixture may be similarly calculated. These calculations are stated in detail later in this calculation note.

2.4 Equilibrium Partitioning Theory, Mass Balance and Volume Conservation

Equilibrium Partitioning Theory assumes that a compound will partition (distribute) linearly between three separate phases in the soil media. The four mass states include the aqueous state, e.g., dissolved in groundwater or soil-pore water; the solid state, e.g., sorbed on soil particles; vapor state, e.g., vapor in the soil pore-air; and NAPL state, as free product, if any NAPL is present in the sample. The explicit partitioning equations will be stated mathematically in the next section. Because of the assumption of conservation of mass, the partitioning of a compound into each of the four separate states must mass balance with the total mass for each compound within the mixture. Likewise, each of the compounds must then mass balance with the total contaminant mass in the sample. This is expressed by the following equation:

$$M_{ti} = M_{ai} + M_{wi} + M_{si} + M_{ni}$$

Where:

M_{ti} = Total mass of compound i in sample

M_{ai} = Mass of compound i in soil pore air

M_{wi} = Mass of compound i in soil pore-water

M_{si} = Mass of compound i sorbed on soil particles

M_{ni} = Mass of compound i as NAPL

Then:

$$M_t = \sum M_{ti}$$

Where:

M_t = Total mass of contaminants in the sample

Application of the equilibrium partitioning calculations and mass conservation equations will permit estimation of the concentrations and masses for each of the chemical compounds in each of the four states. This assumes that an organic compound will partition into the media according to a water-soil (K_d) and a water-vapor (H' Henry's Law constant) distribution coefficient.

All equilibrium calculations use the soil pore-water concentration as the basis for all subsequent equilibrium calculations. The soil pore-water will be one of three permutations in the model:

- the aqueous solubility limit for a single compound NAPL,
- the effective solubility limit for a of compound in a mixture, or
- an estimated pore-water concentration if there is no NAPL in the sample.

The model uses logic arguments to determine which permutation should be used for the equilibrium calculations. Once the pore-water concentration is solved, partitioning calculations are performed to estimate soil pore vapor, sorbed soil, and NAPL concentrations. The mass present in each state is then calculated after concentrations have been determined.

The Soil Saturation Limit or C_{sat} is a type of partitioning equation. C_{sat} is a theoretical upper-bound soil limit that partitions contaminants in three phases only, e.g., soil particles, soil pore air, and soil pore water. It is a threshold mass that defines soil media at the saturation point for contaminant sorbed to soil particles, maximum dissolved contaminant in pore-water and saturation of pore-air with contaminant vapor. For a single chemical compound, NAPL may be present at concentrations exceeding C_{sat} or for a multi-component mixture, NAPL may be present when total mass in the sample exceed the sum

of C_{sat} (Brost et al. 2000). The software will always calculate C_{sat} using either the pure-phase solubility limit or the effective solubility limit.

Partitioning in the saturated zone is managed in a slightly different manner by the software. Since the model assumes there is no air-filled porosity in the saturated zone (all the pore spaces are filled with water), a compound in a saturated sample cannot partition into the vapor phase. Therefore, there can be no C_a in a saturated sample; hence, M_a is deleted from the mass balance equation for saturated samples. In this case, the software will then solve for three states of mass instead of four states.

A reversible partitioning coefficient is used to describe the sorption of the compound from water to organic carbon in the soil. A form of the Freundlich equation (USEPA 1996) is used as a linear isotherm with respect to sorption onto soil. The dimensionless form of Henry's Law Constant is used to describe the partitioning of a compound from the water phase to the vapor phase at a constant 20 degrees C since subsurface soil systems usually maintain a constant temperature.

In order to determine the phase volumes in a sample, the compounds must first be partitioned into the vapor, aqueous, soil, and NAPL phases (if present) of the sample. The volume conservation equation is

$$V_t = V_v + V_w + V_s + V_n$$

Where:

V_t = Total volume of sample

V_a = Volume of soil-pore air

V_w = Volume of soil-pore water

V_s = Volume of soil particles

V_n = Volume of NAPL

Also, where n_t is the total porosity:

$$n_t = \theta_a + \theta_w$$

For saturated samples:

$$n_t = \theta_w \text{ and } \theta_a = 0$$

The partitioning equation for determining the soil saturation limit is expressed as:

$$C_{\text{sat}} = (S_i^E/P_b) * (K_d * P_b + \theta_w + H' * \theta_a)$$

Where:

C_{sat} = Soil Saturation Limit (mg/kg)

S_i or (S_i^E) = Solubility limit of compound in water (mg/L)

P_b = Bulk density (kg/L) *Note: This a computed value performed by the software.

K_d = Soil-water partitioning coefficient (L/kg)

θ_w = Water filled soil porosity (fraction, %)

H' = Henry's Law Constant (dimensionless)

θ_a = Air-filled porosity (fraction, %)

As explained previously, the C_{sat} value represents the chemical-physical saturation limits in soil based on the chemical characteristics of the compound. The value of C_{sat} is the contaminant concentration in soil at which soil-pore vapor and pore water have been

saturated with the chemical and the sorptive limits of the soil particles have been reached. Above this threshold the contaminant may be present in free-phase. Therefore, the mathematical expression used to determine the mass of NAPL for compound i within the sample is

$$\text{NAPL}_i = C_{ti} - C_{\text{sati}}$$

Where:

NAPL_i = Non-aqueous phase liquid for compound i (mg/kg)

C_{ti} = Measured mass for compound i in soil sample (mg/kg)

C_{sati} = Soil Saturation Limit for compound i (mg/kg)

If $C_{ti} < C_{\text{sati}}$, there is no NAPL in the sample.

Because the volume of a sample is composed of solids (soil particles) and void space (porosity), the NAPL must occupy physical space within a sample (Mariner et al). NAPL saturation (S_r) is a calculated value that expresses the volume of residual NAPL saturation within a soil sample. Therefore the residual saturation is defined as the volume fraction of pore space occupied by NAPL. Residual saturation is a useful measurement used to understand the magnitude of NAPL volume in the subsurface. The residual saturation is an important parameter to estimate the potential volume of contaminated media at a waste site for design of a remediation system and as a contaminant baseline against which to measure remediation system performance. Residual saturation is also important to estimate NAPL mobility in the subsurface (Brost et al. 2000).

The residual NAPL saturation equation is

$$S_r = N_v/n_t$$

Where:

S_r = Residual NAPL saturation in soils (% , L/L)

N_v = NAPL volumetric content ($NAPL_t * P_b/P_{napl}$) (% , L/L)

$NAPL_t = \bullet_{NAPLi}$ (mg/kg)

P_{napl} = Density of the NAPL mixture (mg/L)

P_b = Bulk density of soil (kg/L)

n_t = Total volumetric soil porosity (% ,L/L)

2.5 Operational and Computation Order

The following paragraphs describe the computations that are performed in the EXCEL© executable spreadsheet that accompanies this document. The determination of NAPL in a soil sample requires an orderly series of computational steps to be performed. These steps are referred to as an “operational order.” As indicated by the name, a series of computations must be performed in a specific order to arrive at a solution. Some computations in the model are iterative, such as the bulk density, but most are not. However, this does require the “Calculation” option in Excel to be set to “On” to enable iteration a maximum of five times for the model. Use of this feature also enables elimination of “Circular References.” in the calculations.

The operational order for the computations in the model is listed below:

1. The organic chemicals to be evaluated are selected.
2. The concentrations (mass per unit volume) from the analytical results of the soil sample are entered. The units must be in mg/kg or parts per million.

3. The total porosity, air-filled porosity, water-filled porosity, and fraction of organic carbon representative of the soil sample are entered. The units for these values should be entered as decimal fractions. As an example, 40% total porosity equals 0.4. These are the last user-supplied inputs. All physical parameter values are automatically entered by the software from the built-in database.
4. The mole fraction for each compound is calculated.
5. The density of the mixture is calculated.
6. The total solubility of the mixture and the effective solubility of each compound in the mixture is calculated. If there is a single compound in the sample, the pure-phase aqueous solubility limit is used instead.
7. The total vapor pressure of the mixture and the effective vapor pressure of each compound in the mixture is calculated.
8. A theoretical pore-water concentration (IC_{wi}) is calculated. This value is compared to the effective solubility (S^{Ei}) or the solubility limit (S). The software selects the lesser of the effective solubility, solubility limit, or the pore-water concentration to calculate media phase concentrations and masses.
9. C_{sat} is calculated using the effective solubility, solubility limit, or pore-water concentration for each compound.
10. The equilibrium concentration for each compound is calculated for soil pore-water and soil pore-vapor with either the effective solubility limit, or the theoretical pore-water concentration of each compound (IC_{wi}). The software automatically uses a logic function to select the lower of the values S , S^{Ei} or IC_{wi} .

11. The mass per unit volume (M_{ti}) for each compound is calculated for soil pore-water, soil pore-vapor, soil pore-water, and NAPL, if any, based upon the C_{wi} (determined in the preceding step).
12. The mass balance calculations are performed. This equation assumes the form of $(C_i - C_{sati})$, with the NAPL mass being summed for all compounds.
13. The “Percent Residual NAPL Saturation” (S_r) is calculated. This is in the form of a volumetric calculation of either the volume of NAPL occupying air-porosity volume in unsaturated samples or the volume of NAPL occupying total porosity volume for saturated samples. A logic equation is automatically used to determine which.
14. The volume conservation equation is completed to account for all compound mass per volume in the sample, which culminates in a wet bulk density value in units of kg/L. This is an iterative equation and calculates the mass per discrete unit volume for NAPL volume, air-filled porosity volume, water-filled porosity volume, soil volume, and, finally, wet bulk density for the sample.
15. Automatic graphing functions are built-in, including the molar fraction for each compound in the NAPL mixture, the effective solubility for each compound in the NAPL mixture, and the effective vapor pressure for each compound in the NAPL mixture.

3.0 INPUTS

Inputs will be used to operate the software and to check the validity and accuracy of the output. Two separate simulations with different inputs will be used to verify the solutions and ensure software operation. The inputs for the case scenarios are included in Tables 4, 5, 6, and 7.

Table 4. Chemical Properties for Case Scenario #1, #2 and #3

Chemical	Molecular Weight (MW _i) (g/mol)	Solubility Limit (S _i) (mg/L)	Vapor Pressure (VP _i) (mmHg)	Henry's Law Constant (H _i ') (unitless)	Organic Carbon Coefficient (K _{oc}) (L/kg)	Density (d _i) (kg/L)
Trichloroethylene	131.29	1100.0	74.31	0.3649	126.0	1.46
Tetrachloroethylene	165.85	200.0	18.47	0.943	364.0	1.63
Arochlor 1260	372.00	0.0144	0.000011	0.01025	6,700,000.0	1.566
1,3,5-Trinitrobenzene	213.12	385.0	0.00000303	9.1E-8	20.0	1.5
2,4,6-Trichlorophenol	1.97.44	434.0	0.012	0.00019762	2000.0	1.5
Benzo(a)pyrene	252.09	0.00005	5.6E-9	0.0015252	5,500,000.0	0.9

Table 5. Case Scenario #1 - Soil Concentration and Geotechnical Inputs

Chemical	Mass of Contaminant In Sample (C _t , mg/Kg)	Total Porosity (n _t , %)	Volumetric Water Content (• _w , %)	Volumetric Air Content (• _a , %)	Fraction Organic Carbon (F _{oc} , %)
Trichloroethylene	100	40	30	10	0.0001
Tetrachloroethylene	15	40	30	10	0.0001
Arochlor 1260	60	40	30	10	0.0001
1,3,5-Trinitrobenzene	3	40	30	10	0.0001
2,4,6-Trichlorophenol	2	40	30	10	0.0001
Benzo(a)pyrene	1	40	30	10	0.0001

Table 6. Case Scenario #2 - Soil Concentration and Geotechnical Inputs

Chemical	Mass of Contaminant (C _t , mg/Kg)	Total Porosity (n _t , %)	Volumetric Water Content (• _w , %)	Volumetric Air Content (• _a , %)	Fraction Organic Carbon (F _{oc} , %)
Trichloroethylene	10000	42	22	20	0.01
Tetrachloroethylene	14000	42	22	20	0.01

Arochlor 1260	4000	42	22	20	0.01
1,3,5-Trinitrobenzene	10000	42	22	20	0.01
2,4,6-Trichlorophenol	5000	42	22	20	0.01
Benzo(a)pyrene	2500	42	22	20	0.01

Table 7. Case Scenario #3 - Soil Concentration and Geotechnical Inputs for Saturated Sample

Chemical	Mass of Contaminant (C _{ti} , mg/Kg)	Total Porosity (n _t , %)	Volumetric Water Content (• w, %)	Volumetric Air Content (• a, %)	Fraction Organic Carbon (Foc _i , %)
Trichloroethylene	59	40	40	0.0	0.0001
Tetrachloroethylene	977	40	40	0.0	0.0001

4.0 ANALYTICAL METHODS AND CALCULATIONS

4.1 Equation 1 Molar Fraction (from *Chemistry*, Moeller et al. 1980)

Equation 1a Percent Mass

$$W_{ti} = C_{ti}/M_t$$

Where:

W_{ti} = % Mass for compound i (mg/mg)

C_{ti} = Measured soil contaminant mass for compound i (mg/kg)

$M_t = \sum C_{ti}$, Sum of contaminant masses for all compounds in the sample (mg/kg)

Equation 1b Moles/Gram

$$M_{ci} = W_{ti}/MW_i$$

Where:

M_{ci} = Molar Mass or Moles/Gram for compound i (mol/g)

W_{ti} = % Mass for compound i (g/g)

MW_i = Molecular Weight for compound i (g/mol)

Equation 1c Mole Fraction

$$X_i = M_{ci} / \sum M_{ci}$$

Where:

X_i = Mole Fraction for compound i (%)

M_{ci} = % Molar Mass for compound i (mol/g)

$\sum M_{ci}$ = Sum of molar masses (mol/g)

Equation 1d Sum of Mole Fractions

$$\sum X_i = 1$$

4.2 Equation 2 Density of Mixture

$$d = \sum (X_i * d_i)$$

Where:

d = Density of the mixture (kg/L)

X_i = Mole Fraction (%)

d_i = Density for compound i (kg/L)

4.3 Equation 3 Effective Solubility (Raoult's Law from USEPA 1992 and others)

$$S_i^E = X_i * S_i$$

Where:

S_i^E = Effective Solubility for compound i in mixture (mg/L)

X_i = Mole Fraction for compound i (%)

S_i = Pure-Phase Aqueous Phase Solubility for compound i (mg/L)

Equation 3a Solubility of Mixture

$$S_t = \sum S_i^E$$

Where:

S_t = Solubility of the Mixture (mg/L)

4.4 Equation 4 Effective Vapor Pressure

$$VP_i^E = (X_i * VP_i)$$

Where:

VP_i^E = Effective Vapor Pressure for compound i in mixture (mmHg)

X_i = Mole Fraction (%)

VP_i = Pure-Phase Vapor Pressure for compound i (mmHg)

Equation 4a Vapor Pressure of Mixture

$$VP_t = \sum VP_i^E$$

Where:

VP_t = Total vapor pressure for the mixture (mmHg)

4.5 Equation 5 Theoretical Soil Pore-Water Concentration (Feenstra et al. 1991 and Mariner et al. 1997)

$$IC_{wi} = (C_{ti} * P_b) / (K_{di} * P_b + \sum w + H'_i * \sum a)$$

Where:

IC_{wi} = Theoretical Soil Pore-Water Concentration for compound i (mg/L)

C_{ti} = Mass of contaminant i in soil sample (mg/kg)

P_b = Wet Bulk Density (kg/L) *Note: All bulk density values used in the NAPLator model are computed values from equation 18.

K_{di} = Soil-water partitioning coefficient ($f_{oc} \times K_{oci}$) (L/kg)

K_{oc} = Soil organic carbon/water partitioning coefficient (L/kg)

• ω_w = Water filled soil porosity (%)

H'_i = Henry's Law Constant for compound i (dimensionless)

• ω_a = Air filled soil porosity (%)

4.6 Equation 6 Soil Saturation Limit (C_{sati}) (from USEPA 1996 and Brost et al. 2000)

$$C_{sati} = (S_i^E/P_b) * (K_{di} * P_b + \omega_w + H'_i * \omega_a)$$

Where:

C_{sati} = Soil Saturation Limit for compound i (mg/kg)

S_i^E = Effective solubility limit for compound i (mg/L)

P_b = Wet soil bulk density (kg/L)

K_{di} = Soil-water partitioning coefficient (L/kg)

• ω_w = Water-filled soil porosity (% , L/L)

H'_i = Henry's Law Constant for compound i (dimensionless)

- a = Air-filled soil porosity (% , L/L)

4.7 Equation 7 Volumetric Soil Saturation Limit

$$C_{\text{coni}} = C_{\text{sati}} * P_b$$

Where:

C_{coni} = Volumetric Soil Saturation Limit (mg/L)

C_{sati} = Soil Saturation Limit (mg/kg)

P_b = Wet bulk density (kg/L)

4.8 Equation 8 Soil Pore-Water Concentration

$$C_{\text{wi}} = IC_{\text{wi}} \text{ or } S_i \text{ or } S_i^E$$

Where:

IC_{wi} = Theoretical Soil Pore-Water Concentration for compound i (mg/L) or

S_i^E = Effective Solubility for compound i (mg/L) or

S_i = Solubility Limit for compound i (mg/L)

C_{wi} = is determined from logic tests. For example if $X_i = 1$, S_i will be selected as the soil pore-water concentration. If $IC_{\text{wi}} \geq S_i^E$ then S_i^E will be selected as the soil pore-water concentration.

4.9 Equation 9 Soil Pore-Vapor Concentration

$$C_{\text{ai}} = C_{\text{wi}} * H'_i$$

Where:

C_{ai} = Soil pore-vapor concentration for compound i (mg/L)

C_{wi} = Soil pore-water concentration for compound i (mg/L)

H'_i = Henry's Law Constant for compound i (dimensionless)

4.10 Equation 10 Volumetric Soil Pore-Vapor Concentration at STP

$$C_{avi} = C_{ai} * R * CF * T / (P * MW_i)$$

Where:

C_{avi} = Volumetric soil pore-air concentration for compound i (ppmv)

C_{ai} = Soil pore-vapor concentration (mg/L)

R = Universal Gas Constant (8.31451 Pa m³/(K*mole))

CF = Conversion factor (1E+6 mg/L)

T = Temperature (293.15 K)

P = Pressure (101325 Pa)

MW_i = Molecular weight for compound i (g/mol)

4.11 Equation 11 Soil Sorbed Concentration (Freundlich Linear Isotherm from USEPA 1996 and others)

$$C_{si} = K_{di} * C_{wi}$$

Where:

C_{si} = Soil sorbed concentration for compound i (mg/kg)

K_{di} = Soil-water partitioning coefficient for compound i (L/kg)

C_{wi} = Pore-water concentration for compound i (% , mg/L)

4.12 Equation 12 Contaminant Mass in Soil Pore-Water

$$M_{wi} = (C_{wi} * \theta_w) / P_b$$

Where:

M_{wi} = Mass in soil pore water for compound i (mg/kg)

C_{wi} = Soil pore-water concentration for compound i (mg/L)

θ_w = Water filled soil porosity (% , L/L)

P_b = Wet bulk density (kg/L)

4.13 Equation 13a Contaminant Mass in Soil Pore-Air and Equation 13b Contaminant Mass Sorbed to Soil

$$M_{ai} = (C_{wi} * \theta_a * H'_i) / P_b$$

Where:

M_{ai} = Mass in soil pore-air for compound i (mg/kg)

C_{wi} = Soil pore-water concentration for compound i (mg/L)

θ_a = Air filled soil porosity (% , L/L)

H'_i = Henry's Law Constant for compound i (dimensionless)

P_b = Wet bulk density (kg/L)

Equation 13b Contaminant Mass Sorbed to Soil

$$M_{Si} = C_{wi} * K_{di}$$

Where:

M_{s_i} = Mass sorbed to soil for compound i (mg/kg)

C_{w_i} = Soil pore-water concentration for compound i (mg/kg)

K_{d_i} = Soil-water partitioning coefficient for compound i (L/kg)

4.14 Equation 14 NAPL Mass for Compound

$$NAPL_i = C_{t_i} - C_{sati}, \text{ if } C_{t_i} > C_{sati}$$

Where:

$NAPL_i$ = NAPL mass in soil sample for compound i (mg/kg)

C_{t_i} = Soil mass concentration for compound i ($C_{t_i} = M_{t_i}$) (mg/kg)

C_{sati} = Soil Screening Limit for compound i (mg/kg)

4.15 Equation 15 Mass Balance Equation for Compound

$$M_{t_i} = (\bullet M_{a_i} + M_{w_i} + M_{s_i} + M_{NAPL_i})$$

Where:

M_{t_i} = Total contaminant mass of compound i (mg/kg)

M_{a_i} = Mass in soil pore-air for compound i (mg/kg)

M_{w_i} = Mass in soil pore water for compound i (mg/kg)

M_{s_i} = Mass sorbed to soil for compound i (mg/kg)

$NAPL_i$ = Mass of NAPL for compound i (mg/kg)

4.16 Equation 16 Total Mass of NAPL in Sample

$$NAPL_t = \bullet \bullet NAPL_i$$

Where:

$NAPL_t$ = Total mass of NAPL in soil sample (mg/kg)

$NAPL_i$ = Mass of NAPL for compound i (mg/kg)

4.17 Equation 17 Percent Residual NAPL Saturation

$$S_r = (NAPL_t * P_b/d)/n_t$$

Where:

S_r = Percent Residual NAPL Saturation (%)

$NAPL_t$ = Total mass of NAPL in soil sample (mg/kg)

P_b = Wet bulk density (kg/L)

n_t = Total soil porosity (% , L/L)

d = Density of NAPL mixture (mg/L)

4.18 Equation 18 Volume Conservation Equation for Soil Sample (Wet Bulk Density) from Mariner et al. 1997

$$P_b = (W_v * d_w) + (A_v * d_a) + (S_v * d_s) + (N_v * d)$$

Where:

P_b = Wet bulk density (kg/L)

W_v = Volume of soil pore-water (% , L/L)

d_w = Density of water (1.0 kg/L)

A_v = Volume of soil pore-air volume (% , L/L)

d_a = Density of air (0.0013 kg/L)

S_v = Volume of soil (% , L/L)

d_s = Density of soil (2.65 kg/L)

N_v = Volume NAPL (% , L/L)

d = Density of NAPL (kg/L)

4.19 Equation 19 Volumetric Content of NAPL in Sample

$$N_v = (NAPL_t * P_b) / P_{NAPL}$$

Where:

N_v = NAPL volume (L/L)

$NAPL_t$ = Total mass of NAPL in soil sample (mg/kg)

P_b = Wet bulk soil density (kg/L)

P_{NAPL} = Density of NAPL mixture (mg/L)

4.20 Equation 20 Volumetric Content of Air in Sample

$$A_v = \bullet_a - N_v$$

Where:

A_v = Volume of air in sample (% , L/L)

\bullet_a = Air filled soil porosity (% , L/L)

N_v = NAPL volume (% , L/L)

4.21 Equation 21 Volumetric Content of Water in Sample if $\bullet_a = 0$

$$V_w = \bullet_w - N_v$$

Where:

V_w = Volume of water in sample (% , L/L)

\bullet_w = Water filled soil porosity (% , L/L)*

N_v = NAPL volume (% , L/L),

*If $\bullet_a = 0$, model assumes a saturated sample and $\bullet_w = n_t$

4.22 Equation 22 Volumetric Content of Soil in Sample

$$S_v = 1 - (\bullet_w + \bullet_a + N_v)$$

Where:

S_v = Volume of soil (% , L/L)

\bullet_w = Water filled soil porosity (% , L/L)

\bullet_a = Air filled soil porosity (% , L/L)

N_v = NAPL volume (% , L/L)

5.0 RESULTS

Tables 8 through 13 show the results for case scenarios #1, #2, and #3.

Table 8. Case Scenario #1 Results

SOIL SATURATION LIMIT									
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene	Total		
MW=	131.29	165.85	372	213.12	197.44	252.09		MW	Molecular Weight
Si=	804.3938	17.3665	0.0022	5.2031	4.2208	0.0000		mg/L	Effective Solubility
Kd=	0.0126	0.0364	670.0000	0.0020	0.2000	550.0000		L/kg	Partitioning Coefficient
Ow=	0.3000	0.3000	0.3000	0.3000	0.3000	0.3000		%	Water filled porosity
Oa=	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000		%	Air filled porosity
H=	0.3649	0.9430	0.0103	0.0000	0.0002	0.0015		Unitless	Henry's Constant
Pb=	1.8903	1.8903	1.8903	1.8903	1.8903	1.8903		kg/L	Bulk Density
Csat=	153.3270	4.2547	1.4944	0.8362	1.5141	0.0001		mg/Kg	Soil Saturation Limit
Ccon=	289.8290	8.0425	2.8247	1.5806	2.8620	0.0002	305.1391	mg/L	Soil Saturation Limit

CONCENTRATION PER MEDIA									
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene			
Cav=	35075.3770	2375.3064	0.0015	0.0001	0.1016	0.0000	ppmv	Air Concentration	
Ca=	191.4362	16.3767	0.0000	0.0000	0.0008	0.0000	mg/L	Air Concentration	
Cw=	524.6265	17.3665	0.0022	5.2031	4.2208	0.0000	mg/L	Water Concentration	
Cs=	6.6103	0.6321	1.4940	0.0104	0.8442	0.0001	mg/Kg	Soil Concentration	

MASS PER UNIT VOLUME									
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene	Total		
Ma=	10.1275	0.8664	0.0000	0.0000	0.0000	0.0000		mg/Kg	Mass Air
Mw=	83.2622	2.7562	0.0004	0.8258	0.6699	0.0000		mg/Kg	Mass Water
Ms=	6.6103	0.6321	1.4940	0.0104	0.8442	0.0001		mg/Kg	Mass Soil
NAPL=		10.7453	58.5056	2.1638	0.4859	0.9999	72.9006	mg/Kg	Mass NAPL
Mt=	100.0000	15.0000	60.0000	3.0000	2.0000	1.0000		mg/kg	Total Mass

TOTAL NAPL SATURATION			GRAPHS			Mixture Properties		
d=	1.49	kg/L	Density of NAPL Mixture		831.1865	Solubility of Mixture		
NAPL=	72.90	mg/kg	NAPL Mass		55.9444	Vapor Pressure of Mixture		
Pnapl=	1489972.69	mg/L	NAPL Density					
Sr=	0.00023	fraction	NAPL Saturation					
%Sr	0.0231	%	Residual NAPL Saturation					

VOLUME			
Nv=	0.00009	L/L	NAPL Volume
Av=	0.09991	L/L	Air Volume
Wv=	0.3000	L/L	Water Volume
Sv=	0.60	L/L	Soil Volume
V=	0.40	L/L	Total Porosity
Pb=	1.8903	kg/L	Bulk Density

Table 9. Case Scenario #1 Results

	Contaminant		Molecular		Mole		Mixture		Effective		Effective		Groundwater	
	Mass	Total Mass	Weight	Molar Mass	Fraction	Density	Density	Solubility	Solubility	Vapor Pressure	Concentration			
Chemical Name	Cti, mg/kg	%, g/g	g/mol	mol/g	Xi	d, kg/L	di, kg/L	Si, mg/L	Sei, mg/L	VEPi, mmHg	Cwi, mg/L	Ratio Cwi/Si		
Trichloroethene	100	0.552486188	131.29	0.004208136	0.7313	1.46	1.0677	1100.00000	804.3938	54.3405	524.6265	0.65		
Tetrachloroethene	15	0.082872928	165.85	0.000499686	0.0868	1.63	0.1415	200.00000	17.3665	1.6038	61.2258	3.53		
Aroclor 1260	60	0.331491713	372	0.000891107	0.1549	1.566	0.2425	0.01440	0.0022	0.0000	0.0895	40.15		
1,3,5-Trinitrobenze	3	0.016574586	213.12	7.77711E-05	0.0135	1.50	0.0203	385.00000	5.2031	0.0000	18.6674	3.59		
2,4,6-Trichloropher	2	0.011049724	197.44	5.5965E-05	0.0097	1.50	0.0146	434.00000	4.2208	0.0001	5.5754	1.32		
Benzo(a)pyrene	1	0.005524862	252.09	2.19162E-05	0.0038	0.90	0.0034	0.00005	0.0000	0.0000	0.0018	2927888.59		
	181	1	1079.70	0.005754581	1		1.48997		831.19	55.94		29278937.82		

Table 10. Case Scenario #2 Results

SOIL SATURATION LIMIT							Total			
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene		MW	Molecular Weight	
MW=	131.29	165.85	372	213.12	197.44	252.09				
Si=	330.5131	66.5994	0.0006	71.2630	43.3563	0.0000020		mg/L	Effective Solubility	
Kd=	1.2600	3.6400	67000.0000	0.2000	20.0000	55000.0000		L/kg	Partitioning Coefficient	
Ow=	0.2200	0.2200	0.2200	0.2200	0.2200	0.2200		%	Water filled porosity	
Oa=	0.2000	0.2000	0.2000	0.2000	0.2000	0.2000		%	Air filled porosity	
H=	0.3649	0.9430	0.0103	0.0000	0.0002	0.0015		Unitless	Henry's Constant	
Pb=	1.8378	1.8378	1.8378	1.8378	1.8378	1.8378		kg/L	Bulk Density	
Csat=	469.1358	257.2286	40.9244	22.7833	872.3170	0.1076		mg/Kg	Soil Saturation Limit	
Ccon=	862.1898	472.7414	75.2120	41.8717	1603.1665	0.1977	3055.3791	mg/L	Soil Saturation Limit	

CONCENTRATION PER MEDIA									
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene			
Cav=	22097.3816	9109.1182	0.0004	0.0007	1.0439	0.0000	ppmv	Air Concentration	
Ca=	120.6042	62.8032	0.0000	0.0000	0.0086	0.0000	mg/L	Air Concentration	
Cw=	330.5131	66.5994	0.0006	71.2630	43.3563	0.0000020	mg/L	Water Concentration	
Cs=	416.4465	242.4217	40.9244	14.2526	867.1260	0.1076	mg/Kg	Soil Concentration	

MASS PER UNIT VOLUME							Total			
	Trichloroethene	Tetrachloroethene	Aroclor 1260	1,3,5-Trinitrobenzene	2,4,6-Trichlorophenol	Benzo(a)pyrene				
Ma=	13.1247	6.8345	0.0000068	0.0000070	0.0009	0.0000	mg/Kg	Mass Air		
Mw=	39.5646	7.9724	0.0001	8.5307	5.1900	0.0000023	mg/Kg	Mass Water		
Ms=	416.4465	242.4217	40.9244	14.2526	867.1260	0.1076	mg/Kg	Mass Soil		
NAPL=	9530.8642	13742.7714	3959.0756	9977.2167	4127.6830	2499.8924	43837.5033	mg/Kg	Mass NAPL	
Mt=	10000.0000	14000.0000	4000.0000	10000.0000	5000.0000	2500.0000		mg/kg	Total Mass	

TOTAL NAPL SATURATION			Mixture Properties	
d=	1.51	kg/L	Density of NAPL Mixture	
NAPL=	43837.50	mg/kg	NAPL Mass	511.7324 Solubility of Mixture
Pnapl=	1510597.78	mg/L	NAPL Density	28.4793 Vapor Pressure of Mixture
Sr=	0.12698	fraction	NAPL Saturation	
%Sr	12.6985	%	Residual NAPL Saturation	

VOLUME			
Nv=	0.05333	L/L	NAPL Volume
Av=	0.14667	L/L	Air Volume
Wv=	0.2200	L/L	Water Volume
Sv=	0.58	L/L	Soil Volume
V=	0.42	L/L	Total Porosity
Pb=	1.8378	kg/L	Bulk Density

Table 11. Case Scenario #2 Results

	Contaminant	Percent of	Molecular	Mole	Mixture	Effective	Effective	Groundwater				
	Mass	Total Mass	Weight	Molar Mass	Fraction	Solubility	Vapor Pressure	Concentration				
Chemical Name	Cti, mg/kg	%, g/g	g/mol	mol/g	Xi	d, kg/L	di, kg/L	Si, mg/L	Sei, mg/L	VPEi, mmHg	Cwi, mg/L	Ratio Cwi/Si
Trichloroethene	10000	0.21978022	131.29	0.001674006	0.3005	1.46	0.4387	1100.00000	330.5131	22.3277	7045.1478	21.32
Tetrachloroethene	14000	0.307692308	165.85	0.001855245	0.3330	1.63	0.5428	200.00000	66.5994	6.1505	3624.7569	54.43
Aroclor 1260	4000	0.087912088	372	0.000236323	0.0424	1.566	0.0664	0.01440	0.0006	0.0000	0.0597	97.74
1,3,5-Trinitrobenze	10000	0.21978022	213.12	0.001031251	0.1851	1.50	0.2776	385.00000	71.2630	0.0000	31278.6705	438.92
2,4,6-Trichloropher	5000	0.10989011	197.44	0.000556575	0.0999	1.50	0.1498	434.00000	43.3563	0.0012	248.5123	5.73
Benzo(a)pyrene	2500	0.054945055	252.09	0.000217958	0.0391	0.90	0.0352	0.00005	0.0000	0.0000	0.0455	127047429.71
	45500	1	1079.70	0.005571357	1		1.51060		511.73	28.48		127048047.84

Table 12. Case Scenario #3 Results

SOIL SATURATION LIMIT											
	Tetrachloroethene	Trichloroethene	NONE	NONE	NONE	NONE	Total	MW	Molecular Weight		
MW=	165.85	131.29						mg/L	Effective Solubility		
Si=	9.1248	1049.8136						L/kg	Partitioning Coefficient		
Kd=	0.0364	0.0126						%	Water filled porosity		
Ow=	0.4000	0.4000	0.4000		0.4000	0.4000	0.4000	%	Air filled porosity		
Oa=								Unitless	Henry's Constant		
H=	0.9430	0.3649						kg/L	Bulk Density		
Pb=	1.9916	1.9916	1.9916		1.9916	1.9916	1.9916	mg/Kg	Soil Saturation Limit		
Csat=	2.1648	224.0746						mg/L	Soil Saturation Limit		
Ccon=	4.3114	446.2698					450.5812	mg/L	Soil Saturation Limit		
CONCENTRATION PER MEDIA											
	Tetrachloroethene	Trichloroethene	NONE	NONE	NONE	NONE		ppmv	Air Concentration		
Ca=								mg/L	Air Concentration		
Cw=	9.1248	1049.8136						mg/L	Water Concentration		
Cs=	0.3321	13.2277						mg/Kg	Soil Concentration		
MASS PER UNIT VOLUME											
	Tetrachloroethene	Trichloroethene	NONE	NONE	NONE	NONE	Total	mg/Kg	Mass Air		
Ma=								mg/Kg	Mass Water		
Mw=	1.8326	210.8469						mg/Kg	Mass Soil		
Ms=	0.3321	13.2277						mg/Kg	Mass NAPL		
NAPL=	56.8352	752.9254					809.7606	mg/Kg	Mass NAPL		
Mt=	59.0000	977.0000						mg/kg	Total Mass		
TOTAL NAPL SATURATION							GRAPHS		Mixture Properties		
d=	1.47	kg/L	Density of NAPL Mixture						1058.9384	Solubility of Mixture, mg/L	
NAPL=	809.76	mg/kg	NAPL Mass						71.7624	Vapor Pressure of Mixture, mmHg	
Pnapl=	1467756.08	mg/L	NAPL Density								
Sr=	0.00275	fraction	NAPL Saturation								
%Sr=	0.2747	%	Residual NAPL Saturation								
							NAPL in SAMPLE		YES		
VOLUME											
Nv=	0.00110	L/L	NAPL Volume								
Av=		L/L	Air Volume								
Wv=	0.3989	L/L	Water Volume								
Sv=	0.60	L/L	Soil Volume								
V=	0.40	L/L	Total Porosity								
Pb=	1.9916	kg/L	Bulk Density								

Table 13. Case Scenario #3 Results

	Contaminant	Percent of	Molecular		Mole		Mixture		Effective	Effective	Groundwater	
	Mass	Total Mass	Weight	Molar Mass	Fraction	Density	Density	Solubility	Solubility	Vapor Pressure	Concentration	
Chemical Name	Ci, mg/kg	% g/g	g/mol	mol/g	Xi, %	d, kg/L	di, kg/L	Si, mg/L	Si ^E , mg/L	VP ^E , mmHg	Cwi, mg/L	Ratio Cwi/Si
Tetrachloroethene	59	0.056949807	165.85	0.000343381	0.0456	1.63	0.0744	200.00000	9.1248	0.8427	248.6909	27.25
Trichloroethene	977	0.943050193	131.29	0.007182955	0.9544	1.46	1.3934	1100.00000	1049.8136	70.9197	4577.3504	4.36
NONE												
NONE												
NONE												
NONE												
	1036	1	297.14	0.007526337	1		1.46776		1058.94	71.76		

6.0 CONCLUSIONS

The three case scenarios have demonstrated the robust type and quantity of information generated in the software output. The scenarios determined if NAPL was present in a soil sample, and if it was present, the residual saturation, NAPL mass, and NAPL volume were calculated.

The first output calculated the mole fraction for each compound in a chemical mixture. The mole fraction determines the effective solubility for each compound in the mixture as well as the effective vapor pressure and density. The mole fractions balanced accordingly ($X_i = 1$). The effective solubility, theoretical groundwater concentration, or aqueous solubility limit is the first key piece of data for determining if NAPL is present in a mixture of organic compounds.

In a sequential series of calculations, the theoretical pore water concentration was estimated. The theoretical pore water concentration was compared to the effective solubility or solubility of a compound. If the theoretical pore water concentration was less than the effective solubility, the result indicated there was no NAPL in the sample for that particular compound. In this case, mass and concentration were calculated for three phases of soil media: soil, aqueous, and vapor. If the theoretical pore water concentration was greater than the effective solubility, the result indicated NAPL was present in the sample. In this case, mass and concentration was calculated for four phases of mass: soil, aqueous, vapor, and NAPL.

The solubility limit (or effective solubility in the case of a mixture) is used to calculate C_{sat} . C_{sat} is a theoretical limit that indicates when the concentration in soil-pore air and soil pore water and the sorptive limits of the soil particles have been reached. Above this theoretical limit, the contaminant maybe present as free-product. Therefore, C_{sat} is the fundamental parameter used to determine if NAPL is in the sample because it is used to

perform the equilibrium mass balance. Any contaminant mass above the C_{sat} value is NAPL by definition ($C_{\text{ti}} - C_{\text{sati}} = \text{NAPLi}$, if $C_{\text{ti}} \geq C_{\text{sati}}$).

The software next calculated the equilibrium concentrations for pore water, air and soil media using either the smaller of the solubility, effective solubility, or the theoretical pore water concentration as the upper boundary for media phases. The organic compounds were partitioned to three phases of soil media: air, water and soil. Partitioning is derived from a linear isotherm using the Freundlich equation.

The soil pore water concentration was used to calculate the mass of each compound in each phase and subsequently each state according to equilibrium partitioning theory. In the preceding step, C_{sat} was used to determine the mass of NAPL in the sample. The state masses for each compound were summed, including the NAPL mass (if NAPL was in the sample), using the mass conservation equation. Therefore, mass was calculated and balanced for four states (if NAPL was present) and for three states if NAPL was not present. The summed state masses were balanced to the initial measured mass from the soil sample, so the equation balanced precisely ($C_{\text{ti}} = M_{\text{ti}}$) with no statistical residual either + or -.

The total NAPL mass in the sample was then converted into a volume and then reported as a volume fraction. Since volume conservation applies in this model, the NAPL volume fraction is subtracted from the air-filled porosity volume fraction for unsaturated samples because the NAPL must occupy available space (porosity) within the sample. The volume conservation equation balanced precisely $\bullet_t = (N_v + A_v + W_v)$ for porosity in the sample and $V_s = (1 - (N_v + A_v + W_v))$ for solids in the sample. For saturated samples ($O_a = 0$), the NAPL volume fraction is subtracted from the water-filled porosity volume fraction, $V_s = (1 - (N_v + W_v))$ and subsequently $V_t = (N_v + W_v + S_v)$.

This software and calculation method can be extremely powerful for environmental professionals who must determine if NAPL is present in any phase of environment media by evaluating environmental analytical samples. The software is flexible enough to

determine the presence of NAPL in any sample from any phase concentration. For example, if soil vapor sampling is being performed, the soil vapor results (in units of either mg/L or ppmv) can be compared to the vapor concentrations in the model by entering “What-If” soil concentrations into the model. Next, the soil concentrations are adjusted until the soil vapor result equals or exceeds the calculated soil vapor concentration. When the soil vapor computation (C_{ai}) in the model equals the analytical soil vapor concentration results, it may be assumed that all other phases are in equilibrium and equal to all other computed phase concentrations in the model. Similarly, the total concentration of the compound in soil (C_{ti}) can be adjusted to match the concentration collected in the field with any media phase type of analytical data. The total compound concentrations can then be compared to determine relative compound concentrations in any phase.

The software was also useful to quantify the volume of NAPL (S_r) contamination which is widely used as a measure of the quantity present in the environment. NAPL saturation has become the major parameter for measuring the magnitude of NAPL has become more or less a standard used by the scientific community for such. Residual saturation may also be used to assess whether the NAPL may be mobile or immobile (Brost et al. 2000). The volume and density results provide investigators with a number of useful parameters to help estimate the chemical characteristics of contaminated media at a waste site. Likewise, the parameters generated by the software can provide essential data for remedial system design.

This software provides a powerful and robust method of assessing the magnitude of NAPL contamination at a variety of waste sites in all media phases. Use of this model should save both time and money by eliminating the tedious calculations and lookup values needed to perform this analysis. Additionally, the extent of contamination at a waste site may be better estimated using this software. Use of the software in conjunction with the characterization data can result in a detailed development of the subsurface volume of contamination. This will allow the establishment of a baseline against which a remedial system can be designed and its performance assessed.

7.0 REFERENCES

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