ESTCP

USER GUIDE

Source Control and Remedial Performance Evaluation (SCARPE)

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14. ABSTRACT

Two tools were developed to estimate transient mass discharge from a non-aqueous phase liquid (NAPL) source zone, based on a volume-averaged approach. Different models are supplied for single component NAPL (SCARPEs) and multi-component NAPL (SCARPEm). These tools were developed as beta prototypes as part of the Environmental Security Technology Certification Program (ESTCP) project Evaluating and Applying Site-Specific NAPL Dissolution Rates during Remediation (ER19-5223) to support remedial decisions. More information is available at ER19-5223 Project Overview (serdp-estcp.org).

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SOURCE CONTROL AND REMEDIAL PERFORMANCE EVALUATION (SCARPE)

USER MANUAL (revised 16-Jan-2023)

Single-Component NAPL Remediation Tool (SCARPEs v0.1 beta version)

Multi-Component NAPL Remediation Tool (SCARPEm v0.1 beta version)

Two tools were developed to estimate transient mass discharge from a non-aqueous phase liquid (NAPL) source zone, based on a volume-averaged approach. Different models are supplied for single component NAPL (SCARPEs) and multi-component NAPL (SCARPEm). These tools were developed as beta prototypes as part of the Environmental Security Technology Certification Program (ESTCP) project *Evaluating and Applying Site-Specific NAPL Dissolution Rates during Remediation* (ER19-5223) to support remedial decisions. More information is available at ER19-5223 Project Overview (serdp-estcp.org).

Details, background and equations for the single component model (SCARPEs) are provided in a recent publication, "Upscaled Modeling of Complex DNAPL Dissolution", Journal of Contaminant Hydrology, 244(5):103920 (http://dx.doi.org/10.1016/j.jconhyd.2021.103920).

Details, background and equations for the multi-component model (SCARPEm) are under review for an upcoming publication, "Upscaled Modeling of Complex DNAPL Dissolution", currently under review by Groundwater Monitoring & Remediation. The theory, governing equations and limitations for this model are described in the section on model execution.

The Single-Component NAPL Remediation Tool (SCARPEs v0.1) and Multi-Component NAPL Remediation Tool (SCARPEm v0.1) are provided as beta versions and can be downloaded from SCARPEmodel.com or obtained by request from **bo@praxis-enviro.com**. Please email feedback, suggestions, or questions to **bo@praxis-enviro.com**. The models have not been reviewed by ESTCP and do not necessarily represent the view of ESTCP. The SCARPE models have been tested by the authors; however, no responsibility is assumed by the authors for any bugs, deficiencies, or other effects of using these tools. Further, the calculations are based on simplifying assumptions and users expressly agree that the use of the tools is at their sole risk.

This manual is organized in three parts:

1. **SCARPEs NAPL DISCHARGE TOOL** – Single Component NAPL
   a. Tool Inputs
   b. Tool Outputs
   c. Limitations and Errors

2. **SCARPEm NAPL DISCHARGE TOOL** – Multi-Component NAPL

3. **THEORETICAL DISSOLUTION ENHANCEMENT FACTORS**

1.   SCARPEs NAPL DISCHARGE TOOL – Single Component NAPL

The model is written in python and the executable runs in Windows. Double-click on the executable file to start (note that the executable may take a few minutes to start), then select the input file. An example input file is provided with the model download (example_input.xlsx). Details for preparing input files are described in the next section. Input and output folders are automatically created in the folder containing the executable file if these folders do not exist.

The interface screen indicates successful import of the data and calculations are performed automatically (see **Figure S.1**). When calculations are complete, a message appears on the interface screen and the model generates output placed in an output folder as described later.
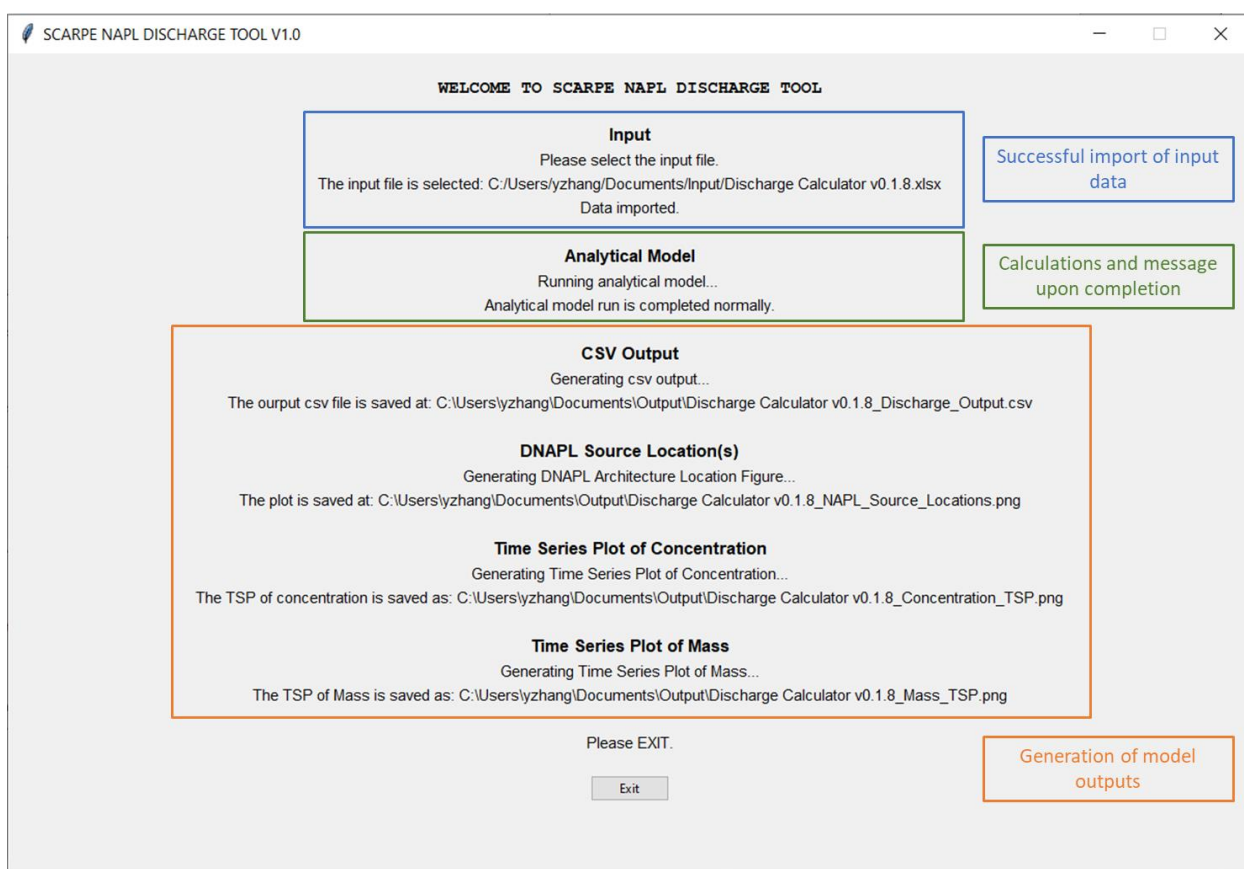
Figure S.1 – Interface Screen

To perform and save output from multiple runs, the input file name must be changed for each run to save each output file separately, or the output file names must be edited between runs. The model executable automatically writes over an existing output file if the input file name is not changed. In addition, the Excel input file must be closed to enable reading of input data by the executable file. It is recommended to create a separate file for tracking input parameters and associated output file names.

Tool Inputs

Input Data File

The NAPL Discharge Tool utilizes an excel file for data input and simplifies the formatting process. A template input file (**Example_Input.xlsx)** is provided with the executable and should be placed in the input folder. The template excel file is protected and only displays one tab specifying the input variables (see **Figure S.2**). The yellow highlighted cells are the required user inputs. Other calculated values, e.g., NAPL saturation, are displayed for reference in formulating input data. An approximation for the time for each NAPL mass to be fully depleted is provided in the row titled "Time to Depletion."

Single-Component NAPL Remediation Tool (SCARPEs v0.1) — Beta Version

Source Zone Parameters

Length (X_s)	m	0.4	$X_{s,0}$	0
Width (Y_s)	m	0.0254	$Y_{s,0}$	0
Height (Z_s)	m	0.195	$Z_{s,0}$	0
Darcy Velocity (U_0)	m/day	0.9757149		
Porosity	-	0.4495		
Fraction Mobile (f_m)	-	0.5		
Porosity Immobile	-	0.33		
K_{im}	1/day	2		
$S_{irreducible}$	-	0.15		
k_r exponent	-	3		
Volumetric Flow (Q)	L/day	4.8327158		
Source Volume (V_s)	m³	0.0019812		

Enter parameters in yellow cells
White cells are calculated automatically
Cells under Mass 1 must be entered; other mass cells can be empty

NAPL Component Parameters — TCE

Density (ρ_i)	g/L	1460
Solubility (C_i^*)	mg/L	1100
Molecular Weight	g/mol	131
Diffusion Coefficient	cm²/day	0.6048
Retardation (R_i) - Mobile		1.1
Retardation (R_{im}) - Immobile		1.1
C inlet ($C_{0,i}$)	mg/L	0
1st Order Decay-Mobile	1/day	10
1st Order Decay-Immobil	1/day	0
Initial Conc - Mobile	mg/L	10
Initial Conc - Immobile	mg/L	0

Solution Settings

Total Time	days	30
Printing Time Interval	days	0.1

NAPL Architecture		Mass 1	Mass 2	Mass 3	Mass 4	Mass 5	Mass 6	Mass 7	Mass 8	Mass 9	Mass 10
M_{napl} (M_n)	g	9.928	7.3								
Start Location $X_{a,0}$	m	0.17	0.095								
Length X_a	m	0.075	0.35								
Start Location $Y_{a,0}$	m	0	0								
Width Y_a	m	0.0254	0.0254								
Start Location $Z_{a,0}$	m	0.01	0								
Height Z_a	m	0.185	0.005								
Is A_{xy} double-sided?	1 or 2	1	1								
Dispersivity (σ_T)	m	0.001	0.001								
Enhancement?	-	1	1								
gamma (γ)	-	0.5	0.5								
a_d (0 < a_d <= 1)	-	0	1								
Time to Depletion	days	2.006993	11.938418	0	0	0	0	0	0	0	0
Impacted Volume (V_a)	m³	0.0003524	4.445E-05	0	0	0	0	0	0	0	0
Saturation (S_n)	-	0.0429	0.2502	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Number of DNAPL Masses		2	Number of DNAPL Components		1	Number of Soil Domains		2		

Figure S.2 – Excel Input File Interface

Variables are defined in four categories:

- Source Zone Parameters – define the geometry and characteristics of the overall source zone

- NAPL Component Parameters – define the properties and problem-specific characteristics of the single NAPL component

- Solution Settings – define the total time for simulation and printing interval for output

- NAPL Architecture – define the mass, geometry and dissolution characteristics of each NAPL accumulation within the source zone (a minimum 1 mass is required)

Description of Input Variables

The primary characteristic features defining the NAPL dissolution and discharge problem are illustrated in **Figure S.3**. The source zone dimensions (X_S, Y_S, Z_S) fully encompass the NAPL accumulations considered with a height that generally coincides with the height of discharge measurement (e.g., a groundwater monitoring or pumping well screen). The Darcy velocity, U_0, is in the x-direction and defines the total flow, Q, through the source zone where $Q = U_0 Y_S Z_S$. Each NAPL accumulation is assumed to have a relatively uniform saturation defined by its mass (M_a), its characteristic sub-volume ($V_a = X_a Y_a Z_a$) and the total soil porosity. Additional parameters for the NAPL dissolution model (α_T and γ) are described below in **Table S.1**.

Simple estimates for remedial impacts can be generated with technology-specific enhancements and first order reaction rates. An enhancement factor can be specified as indicated in **Table S.1** and is applied to the NAPL dissolution rate. The potential enhancement is expected to depend on the flow rate compared to the natural gradient, the reaction rate, and NAPL architecture. For example, when groundwater pumping is performed the characteristic velocity through the source zone increases and the ratio to the natural flow provides the enhancement factor. Additional details on estimating flow enhancements and reactive enhancements can be found in the Final Report for ER19-5223 available at ER19-5223 Project Overview (serdp-estcp.org).

The tool also includes optional parameters for including an immobile domain (only applicable if $f_m < 1$) to model diffusion into and out of fine-grained material as a first order process.

Additional information and discussion on the parameters can be found in the previously cited publication, "Upscaled Modeling of Complex DNAPL Dissolution."

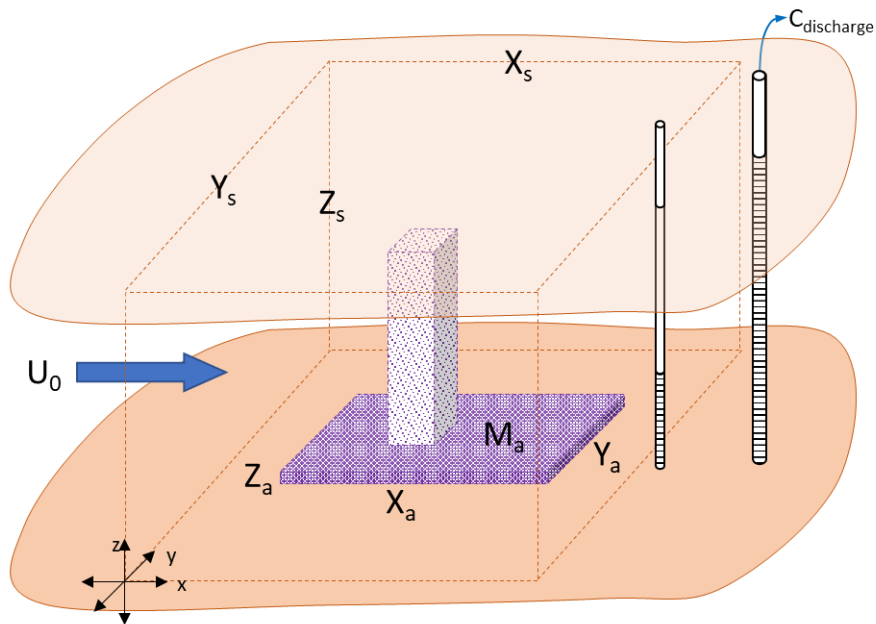**Figure S.3 – Characteristic Dimensions of the Source Zone and NAPL Mass Accumulations**

Units

The units are specified for the input and output files and cannot be modified, i.e., the user needs to enter the variables in the specified units.

Table S.1. Input Variable Descriptions

	Units	Description	Potential Sources of Information and References
Source Zone Parameters			
Length (X_s)	m	Length of the source zone (in groundwater flow direction)	- Estimated longitudinal extent of the complete NAPL footprint based on soil borings, groundwater monitoring data, historical release information, or other characterization tools
Width (Y_s)	m	Width of the source zone (perpendicular to groundwater flow direction)	- Estimated lateral extent of the complete NAPL footprint based on soil borings, groundwater monitoring data, historical release information, or other characterization tools - Can also be based on width of a monitoring transect downgradient of NAPL source zone or the width of the capture zone of a pumping well
Height (Z_s)	m	Height of the source zone	- Estimated NAPL vertical extent based on soil borings, groundwater monitoring data, historical release information, or other characterization tools - Can also be based on downgradient monitoring well screen intervals, monitoring transect vertical extent and/or aquifer thickness
$X_{s,0}$	m	Starting coordinates for NAPL source zone Only use for plotting NAPL source, values do not impact solution	- The origin (0,0,0) is the least confusing option. The values do not impact the solution but non-origin values may be useful for illustration when output is used as transport model input
$Y_{s,0}$	m		
$Z_{s,0}$	m		

Darcy Velocity (U_0)	m/day	Darcy velocity through the NAPL source zone	- Can be estimated based on hydraulic gradient and hydraulic conductivity
			  - Hydraulic gradient can be calculated based on water level contour map(s)
			  - Hydraulic conductivity can be estimated based on aquifer testing data and/or based on soil type and typical range of conductivity values (for example from Freeze and Cherry, Groundwater, 1979 - available at https://fc79.gw-project.org/english/chapter-2/#2.3). If multiple measurements are available, the median or geometric mean can be used to estimate the average within the source zone.

Porosity	-	Porosity of mobile domain (or of entire domain if no immobile domain)	- Can be measured in soil samples - Can be estimated based on soil type and typical range of porosity values (for example from Freeze and Cherry, Groundwater, 1979 - available at https://fc79.gw-project.org/english/chapter-2/#2.5)
Fraction Mobile (f_m)	-	Fraction of mobile domain (between 0 and 1)	- $0 < f_m \leq 1$ (immobile domain fraction is $1 - f_m$) - Default value is 1; model applicability diminishes with decreasing value unless increasing characterization of immobile zones is available
Porosity Immobile	-	Porosity of the immobile domain	- Can be measured in soil samples - Can be estimated based on soil type and typical range of porosity values (for example from Freeze and Cherry, Groundwater, 1979 - available at https://fc79.gw-project.org/english/chapter-2/#2.5)
K_{im}	1/day	Mass transfer coefficient between mobile and immobile domains	- Various physical interpretations can be applied to this first order parameter[1] - This model assumes uniformly distributed lenses of fine-grained material in the source zone wherein aqueous diffusion dominates the mass transfer process. Hence, lens thickness, porosity and surface sorption parameters determine this first order coefficient.
$S_{irreducible}$	-	Irreducible water saturation	- Used to calculate the relative permeability k_r, based on the Wyllie correlation[2,3] - Typically varies from 0.05 to 0.15 depending upon the soil type[4] - Default value is 0.15
k_r exponent	-	Relative permeability exponent	- Used to calculate the relative permeability k_r, based on the Wyllie correlation[2,3] - Default value is 3
Volumetric Flow (Q)	L/day	Total flow through source zone	- Calculated based on U_0, Ys, Zs
Source Volume (V_s)	m^3	Total source volume	- Calculated based on Xs, Ys, Zs

[1] Haggerty, R. and S. Gorelick, 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, Water Resources Research, 31(10) pp 2383-2400, https://doi.org/10.1029/95WR10583
[2] Wyllie, M.R.J., 1962. Relative permeability. In: Frick, T.C., Taylor, R.W. (Eds.), Petroleum Production Handbook, Vol. II, Reservoir Engineering. McGraw-Hill, New York, pp. 25.1–25.14.
[3] This version of the model assumes a constant relative permeability (k_r), equal to the averaged relative permeability based on the initial mass, which is calculated using the Wyllie correlation.
[4] Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W., Hagan, E., 1990. Laboratory Investigations of Residual Organic Liquids from Spills, Leaks, and Disposal of Hazardous Wastes in Groundwater, Rep. EPA/600/6–90/004. Environ. Prot. Agency, Washington, D. C.

	Units	Description	Potential Sources of Information and References
NAPL Component Parameters			
Density (ρ_i)	g/L	NAPL component density	- Can be found in chemical databases (e.g., CompTox Chemicals Dashboard (epa.gov)
Solubility (C_i^*)	mg/L	NAPL component solubility	- Can be found in chemical databases (e.g., CompTox Chemicals Dashboard (epa.gov)
Molecular Weight	g/mol	NAPL component molecular weight	- Can be found in chemical databases (e.g., CompTox Chemicals Dashboard (epa.gov)
Diffusion Coefficient	cm^2/day	NAPL component diffusion coefficient in water at appropriate temperature.	- USEPA on-line tools can be used to estimate diffusion coefficients (https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion.html and https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html)
Retardation (R_i)	-	Retardation factor in mobile soil domain resulting from water-soil partitioning of the NAPL component	- Can be calculated based on $R_i = 1+\rho b*Koc*foc/$(mobile porosity) ρb is bulk density of mobile domain (can be estimated based on $\rho b = 2.65*(1-$mobile porosity) or measured in soil samples; Koc is octanol-water partition coefficient for the NAPL component; and foc is the organic carbon fraction of soil solids in the mobile domain that can be measured in soil samples - USEPA on-line tools can be used for this calculation (https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/retard.html), which include Koc values for several constituents - Koc values can also be found in CompTox Chemicals Dashboard (epa.gov)
Retardation (R_{im}) - Immobile	-	Retardation factor in immobile soil domain	- As above, although ρb, foc, and porosity can be different in the immobile soil domain, e.g., clayey silt versus sand.
C inlet ($C_{0,i}$)	mg/L	Influent NAPL component concentration upgradient of the source zone	- Can be estimated based on groundwater monitoring data although the value is a constant - Default value is 0
1st Order Decay-Mobile	1/day	First-order degradation rate of dissolved phase in mobile domain	- Can be estimated from monitoring data, literature values based on site-specific redox and geochemical conditions, or remedy assumptions - Default value is 0 although increased values can be used to represent remedial processes decreasing the discharge concentration
1st Order Decay-Immobile	1/day	First-order degradation rate of dissolved phase in immobile domain	- Can be estimated from monitoring data or from literature values based on site-specific redox and geochemical conditions - Default value is 0
Initial Conc - Mobile	mg/L	Initial (average) dissolved concentration in mobile domain in the NAPL source zone	- Can be estimated based on groundwater monitoring data - Default value is 0
Initial Conc - Immobile	mg/L	Initial (average) dissolved concentration in immobile domain in the NAPL source zone	- Can be estimated based on groundwater monitoring data - Default value is 0
Solution Settings			
Total Time	days	Total calculation time for tool outputs	- Not applicable
Printing Time Interval	days	Time interval for tool outputs (output variables will be printed at each time interval through total calculation time)	- Not applicable
NAPL Architecture			
M_{napl} (M_n)	g	Mass of NAPL in the accumulation	- Can be estimated based on release information and/or site-specific measurements or can be back-calculated based on estimated saturation
Start Location ($X_{a,0}$)	m	Starting coordinate for individual NAPL accumulation Only used for illustrating the relative locations of NAPL accumulations, values do not impact solution	- As described below for the Inhibition Factor, a mass accumulation upgradient of a second accumulation will inhibit, or suppress, the dissolution of the downgradient mass by decreasing the driving concentration gradient until the upgradient mass depletes. The start locations and lengths yield an illustration of the relative NAPL locations in the output graph "NAPL_Source_Locations.png"
Length (X_a)	m	Length of the NAPL accumulation (in groundwater flow direction)	- Estimated longitudinal extent of the individual NAPL accumulation footprint based on soil boring, groundwater monitoring data, historical release information, or other characterization tools - See Figure 3
Start Location ($Y_{a,0}$)	m	Starting coordinate for individual NAPL accumulation	- See the description for $X_{a,0}$
Width (Y_a)	m	Width of NAPL accumulation (perpendicular to groundwater flow direction)	- Estimated lateral extent of the individual NAPL accumulation footprint based on soil boring, groundwater monitoring data, historical release information, or other characterization tools - See Figure 3
Start Location ($Z_{a,0}$)	m	Starting coordinate for individual NAPL accumulation	- See the description for $X_{a,0}$
Height (Z_a)	m	Height of NAPL accumulation	- Estimated NAPL accumulation footprint based on soil boring, groundwater monitoring data, historical release information, or other characterization tools - See Figure 3

	Units	Description	Potential Sources of Information and References
NAPL Architecture (continued)			
Is A_{xy} double-sided?	1 or 2	Flow on one side (1) or both sides (2) (i.e., above and below) of the NAPL accumulation	- Expected to be 1 for DNAPL; may be 2 for LNAPL; represents the number of surfaces available for tangential dispersion - Default value is 1
Dispersivity (α_T)	m	Tangential Dispersivity	- Default value is 0.001
Enhancement	-	Enhancement factor for NAPL mass transfer	- Default value is 1 and represents natural flow conditions - Can be used to represent remediation options (for example enhanced groundwater flow due to extraction, or enhanced dissolution resulting from increased degradation rates, e.g., enhanced biodegradation or chemical oxidation/reduction)
gamma (γ)	-	Exponent of the mass ratio	- $0 \leq \gamma < 1$ - γ expected to fall between theoretical values of 0.5 (pool) and 0.67 (ganglia) - γ can be used as a fitting parameter with discharge concentration measurements - γ has a significant impact on the depletion tail and little influence on early discharge concentrations
a_d ($0 < a_d \leq 1$)	-	Inhibition factor	- a_d is a shape factor accounting for any overlap of projected areas between the two masses, one upgradient to another. In practice masses are assumed independent ($a_d = 0$) or are directly in line with each other ($a_d = 1$). - Default is 0 (no inhibition) - a_d for Mass 1 is always 0, i.e., no mass is allowed to reside upgradient of Mass 1 - For inhibition of a mass by an upgradient mass, the downgradient mass must follow directly in the input table, i.e., Mass a +1 is inhibited by Mass a as indicated by a nonzero a_d - Inhibition is allowed to be sequential, i.e., multiple masses can reside in line along the flow direction - Changes in flow direction resulting from groundwater pumping or injection can be captured with changes in the shape factor, assuming the relative spatial locations of distinct masses are available.
Time to Depletion	days	Time for depletion of NAPL accumulation	- Calculated based on input parameters - This time is for complete removal of the NAPL mass. This is not expected to be achievable in the field, where residual mass may remain in the subsurface, but this number provides information on the order of magnitude of NAPL source lifetime and is useful for comparison between the different masses, and understanding the impact of the NAPL characteristics on NAPL lifetime.
Impacted Volume (V_a)	m^3	Volume impacted by NAPL accumulation	- Calculated based on Xa, Ya, Za - Sum of accumulation volumes must be less than the mobile source zone volume to avoid overlapping NAPL volumes.
Saturation (S_n)	-	NAPL accumulation saturation	- Calculated for the NAPL impacted volume based on NAPL mass, NAPL density and total porosity

Tool Outputs

Copies of displayed output figures are automatically saved in the output folder. The raw data for discharge concentration and remaining mass are saved in the output folder as a comma-separated value file. The output files are named using the input file name. For example, if the input file name is inputfile1.xlsx, the following output files are saved:

- inputfile1_Output.csv

- inputfile1_NAPL_Source_Locations.png

- inputfile1_Concentration_TSP.png

- inputfile1_Mass_TSP.png

Graphs

The Single-Component NAPL Remediation Tool creates three output graphs saved in the output folder:

- A 3D rendering of the relative locations defining the NAPL source zone (i.e., XXX_ NAPL_Source_Locations.png) – depicts the geometry of the source zone (blue rectangle) and the NAPL accumulations located inside it (black rectangles)
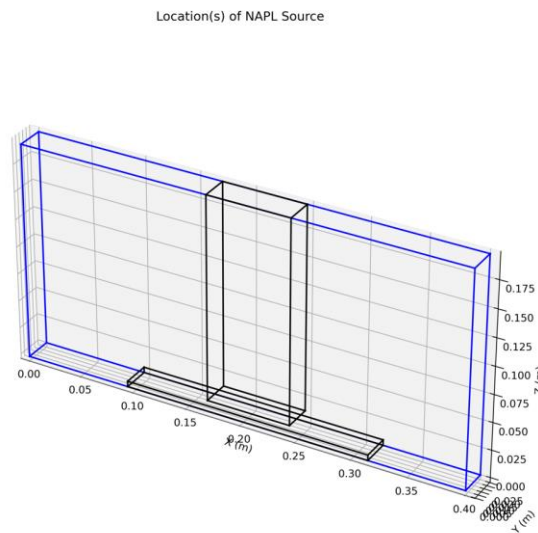

Figure S.4 – Output Graph: NAPL Source Locations

- The time series plot of discharge concentration (i.e., XXX_ Concentration_TSP.png) – plots the discharge concentration over time; the mass discharge is calculated from this concentration multiplied by Q
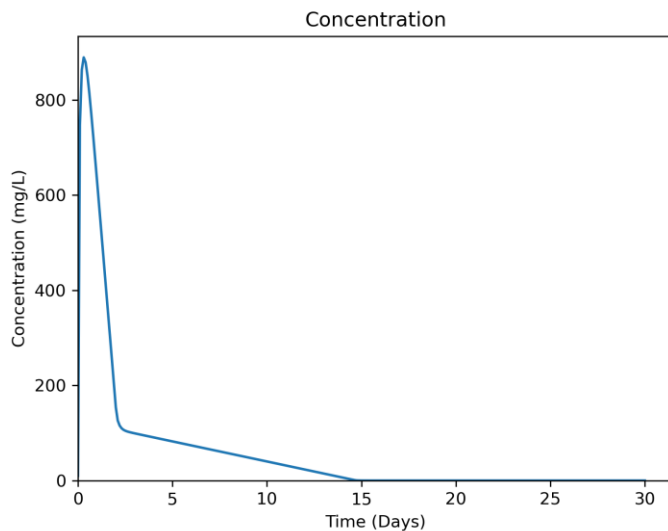
Figure S.5 – Output Graph: Time Series Plot of NAPL Concentration in Discharge

- The time series plot of remaining mass (i.e., XXX_ Mass_TSP.png) – plots the remaining NAPL mass in the source zone over time
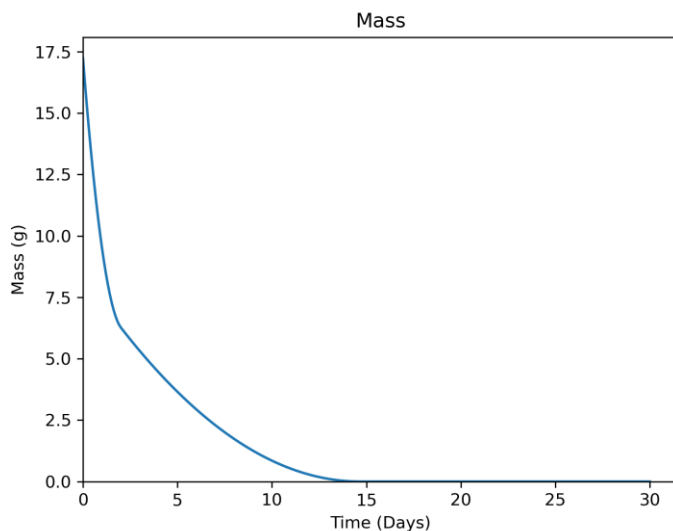

Figure S.6 – Output Graph: Time Series Plot of NAPL Mass in the Source

Output Files

The Single-Component NAPL Remediation Tool saves calculation results into a csv file (XXX_Output.csv) in the output folder. The program will write over an existing file with the same name without warning. The output data structure is shown in **Figure S.7** below. The first three rows

list the time of depletion for each of the NAPL accumulations. The time of depletion is the time for complete (100%) removal of the NAPL mass in the source zone. This is not expected to be achievable in the field, where residual mass may remain in the subsurface, but this number provides information on the order of magnitude of NAPL source lifetime and is useful for comparison between the different masses, and understanding the impact of the NAPL characteristics on NAPL lifetime. The user can use the output file (see below) to estimate cleanup time for different end points (for example based on percentage of NAPL mass removal, target mass discharge or target discharge concentration).

From row four, the calculated results are listed by columns and printed at the specified intervals in rows. The columns of calculated variables are:

- Time – cumulative time (days)

- C – source discharge concentration (gram per cubic meter or mg/L)

- Ci – average aqueous concentration in the immobile domain (gram per cubic meter or mg/L)

- Rmass – remaining NAPL mass in the source zone (grams)

- gen – volumetric mass generation term calculated as the mass discharge rate per unit source zone volume (grams per day per cubic meter)

- Mass Rate – mass discharge from the source zone (grams per day)

	A	B	C	D	E	F
1	Time Deplete (days):					
2	Mass 1	Mass 2				
3	2.006993	14.6571				
4	Time	C	Ci	Rmass	gen	Mass Rate
5	days	mg/L	mg/L	g	g/day/m3	g/day
6	0	10	0	17.228	24.39287	0.048327
7	0.100897	747.2883	381.1429	16.25217	1822.851	3.611432
8	0.201794	863.2963	681.0038	15.32109	2105.828	4.172066
9	0.302691	889.2346	816.3656	14.43479	2169.099	4.297418
10	0.403587	878.7042	862.4371	13.59328	2143.412	4.246527
11	0.504484	849.9197	862.629	12.79657	2073.198	4.10742
12	0.605381	811.8035	839.342	12.0447	1980.222	3.923216
13	0.706278	768.8978	804.0341	11.3377	1875.562	3.715864
14	0.807175	723.5208	762.5608	10.67561	1764.875	3.496571
15	0.908072	676.8548	717.9125	10.05846	1651.043	3.271047
16	1.008969	629.501	671.615	9.486327	1535.534	3.042199
17	1.109865	581.7636	624.4452	8.95925	1419.088	2.811498
18	1.210762	533.7949	576.7972	8.477299	1302.079	2.579679
19	1.311659	485.6697	528.8693	8.040543	1184.688	2.347104
20	1.412556	437.4232	480.7597	7.649057	1067.001	2.113942
21	1.513453	389.07	432.5155	7.302922	949.0534	1.880265

Figure S.7 – Output CSV File

Uses

In addition to providing information on time to NAPL depletion, mass discharge, discharge concentration, and remaining NAPL mass, the outputs from the NAPL Discharge Tool can be used as input to groundwater transport models for evaluating downgradient plume concentrations. Compatible models include:

- MT3DMS or MT3D-USGS three-dimensional numerical model where the mass rate is a mass loading input to represent dissolution from a NAPL source zone; and

- A soon-to-be-released semi-analytical solute transport model for a three-dimensional aquifer with sequential first order decay and dual porosity[5] provided by the United States Environmental Protection Agency. The volumetric mass generation source term in the Discharge Tool output can be directly read as input by the transport model. The model pairing provides a fast, convenient methodology to assess plume changes in response to transient discharge including first approximations for remedial efforts.

LIMITATIONS and INPUT ERROR CHECKING

Limitations

The results generated with the NAPL Discharge Tool are based on several simplifying assumptions resulting in limitations to some field applications. These assumptions are discussed in "Upscaled Modeling of Complex DNAPL Dissolution" and include:

- The NAPL is assumed to be immobile and the potential for partial re-mobilization of NAPL mass during dissolution is not considered.

- This version of the model does not allow changes in flow or degradation rates within the source zone; steady conditions are assumed.

- This version of the model assumes constant relative permeability (k_r), equal to the averaged relative permeability based on the initial mass. This approximation overpredicts early discharge and underpredicts later mass discharge but roughly matches the depletion time for the NAPL mass.

- The flow rate through the source zone and resulting dispersion are assumed to be sufficiently large to render aqueous diffusion negligible in NAPL dissolution.

- Increases in local soil heterogeneity are not explicitly included and are expected to limit the applicability of the model to those conditions, although modifications to the dissolution model can provide approximations.

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[5] Perina, T., 2022. Semi-analytical model for solute transport in a three-dimensional aquifer with dual porosity and a volumetric source term. Journal of Hydrology 607, 127520. https://doi.org/10.1016/j.jhydrol.2022.127520

- The model is not intended to match initial breakthrough curves precisely as a result of volume-averaging in the source zone. The averaging in the upscaled model is expected to yield a lesser peak discharge concentration and to lag the time of the actual breakthrough peak.

- As with all models, limitations in available data for characterizing the source zone directly limit the representativeness of the results; however, the NAPL Discharge Tool is designed to be adaptable for accepting an increased resolution of input data, e.g., an increased number of defined mass accumulations and characterization of fine-grained lenses.

Error Checking

Several conditions can prevent the tool executable from running properly. If the user is not able to run the tool successfully, please check for the following potential conflicts:

- If the program window closes automatically or the interface window does not appear after shortly after double clicking the executable file, check to ensure output file with the same prefix as the input file are closed and available for writing. If not, close the .csv and .png output files and launch the executable file again.

- After selecting the input file, if the input file is open, does not exist, or the program cannot find the input file, the following error message will be displayed in the window.
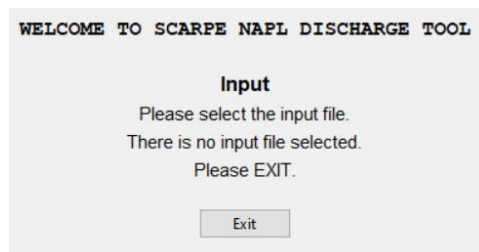

WELCOME TO SCARPE NAPL DISCHARGE TOOL

Input
Please select the input file.
There is no input file selected.
Please EXIT.

Exit

Figure S.8 – Error Message 1

- Please troubleshoot the following items:

  o Make sure the input file is closed.

  o Check the location of the input file and make sure the input file is accessible.

  o After selecting a readable input file, if the following error message pops up on the window, it may include error(s) in the input file. Please double check the input parameters in the input file.
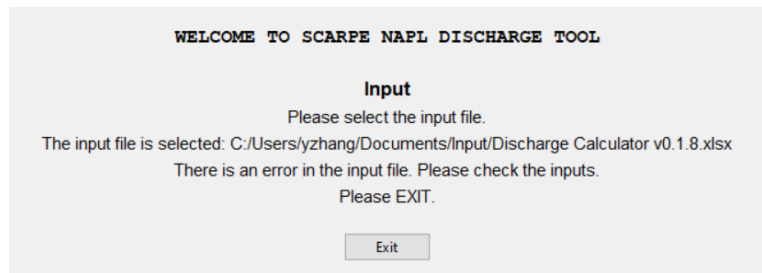
WELCOME TO SCARPE NAPL DISCHARGE TOOL

Input
Please select the input file.
The input file is selected: C:/Users/yzhang/Documents/Input/Discharge Calculator v0.1.8.xlsx
There is an error in the input file. Please check the inputs.
Please EXIT.

Exit

Figure S.9 – Error Message 2

- For some parameters, valid input values must fall within the following ranges (or the above error message will be displayed):

- X_s, Y_s, $Z_s > 0$

- $U_0 > 0$

- Porosity > 0 and < 1

- $f_m > 0$ and ≤ 1

- Porosity Immobile > 0 and < 1

- $K_{im} \geq 0$

- Total Time > 0

- $\rho_i > 0$

- $C_i^* > 0$

- $R_i \geq 1$

- $R_{im} \geq 1$

- $C_{0,i} \geq 0$

- 1st Order Decay-Mobile ≥ 0

- 1st Order Decay-Immobile ≥ 0

- Initial Conc – Mobile ≥ 0

- Initial Conc – Immobile ≥ 0

- For each NAPL architecture:

- Number of DNAPL Masses ≥ 1 (Integer)

- $M_n > 0$

- $X_a, Y_a, Z_a > 0$

- Is A_{xy} double-sided? = 1 or 2

- $\alpha_T \geq 0$

- Enhancement > 0

- $0 \leq \gamma < 1$

- $0 < a_d \leq 1$

In addition, calculated dissolution model parameters must be physically consistent. A number of checks are provided within the excel input spreadsheet for the most common issues, as follows:

- $X_a, Y_a, Z_a \leq X_s, Y_s, Z_s$

- Sum of individual impacted volumes $(\sum V_a) \leq V_s * f_m$

- Each accumulation saturation $(S_n) \leq 1 - S_{irr}$

An error warning appears in the excel input file (column O) if the conditions above are not met, as shown **Figure S.10** below.

Single-Component NAPL Remediation Tool (SCARPEs v0.1)   Beta Version

Source Zone Parameters				
Length (X_s)	m	0.4	$X_{s,0}$	0
Width (Y_s)	m	0.0254	$Y_{s,0}$	0
Height (Z_s)	m	0.195	$Z_{s,0}$	0
Darcy Velocity (U_0)	m/day	0.9757149		
Porosity	-	0.4495		
Fraction Mobile (f_m)	-	0.5		
Porosity Immobile	-	0.33		
K_{im}	1/day	2		
$S_{irreducible}$	-	0.15		
k_r exponent	-	3		
Volumetric Flow (Q)	L/day	4.8327158		
Source Volume (V_s)	m³	0.0019812		

Enter parameters in yellow cells
White cells are calculated automatically
Cells under Mass 1 must be entered; other mass cells can be empty

NAPL Component Parameters		TCE
Density (ρ_i)	g/L	1460
Solubility (C_i^*)	mg/L	1100
Molecular Weight	g/mol	131
Diffusion Coefficient	cm²/day	0.6048
Retardation (R_i) - Mobile		1.1
Retardation (R_{im}) - Immobile		1.1
C inlet ($C_{0,i}$)	mg/L	0
1st Order Decay-Mobile	1/day	10
1st Order Decay-Immobil	1/day	0
Initial Conc - Mobile	mg/L	10
Initial Conc - Immobile	mg/L	0

Solution Settings		
Total Time	days	30
Printing Time Interval	days	0.1

NAPL Architecture		Mass 1	Mass 2	Mass 3	Mass 4	Mass 5	Mass 6	Mass 7	Mass 8	Mass 9	Mass 10	INVALID INPUT?
M_{napl} (M_n)	g	9.928	7.3	20	7.3							
Start Location $X_{a,0}$	m	0.17	0.095	0.095	0.095							ERROR! All Xa must be less than Xs
Length X_a	m	0.075	0.35	0.7	0.35							
Start Location $Y_{a,0}$	m	0	0	0.03	0.06							
Width Y_a	m	0.0254	0.0254	0.0254	0.0254							
Start Location $Z_{a,0}$	m	0.01	0	0	0							
Height Z_a	m	0.185	0.005	0.002	0.15							
Is A_{xy} double-sided?	1 or 2	1	1	1	1							
Dispersivity (σ_T)	m	0.001	0.001	0.001	0.001							
Enhancement?	-	1	1	1	1							
gamma (γ)	-	0.5	0.5	0.5	0.5							
a_d (0 < a_d <= 1)	-	0	1	1	1							
Time to Depletion	days	2.006993	11.938418	29.746792	16.458593	0	0	0	0	0	0	
Impacted Volume (V_a)	m³	0.0003524	4.445E-05	3.556E-05	0.0013335	0	0	0	0	0	0	ERROR! Sum of Va must be less than Vs*fm
Saturation (S_n)	-	0.0429	0.2502	0.8570	0.0083	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	ERROR! All Sn must be less than (1-Sirr)
Number of DNAPL Masses		4	Number of DNAPL Components		1	Number of Soil Domains		2				

Figure S.10 – Example Error Messages in Excel Input File

Execution Time

The run time for the model depends upon the number of masses input and the computer processor. For most scenarios, the run time is less than one minute; however, inclusion of an immobile fraction can result in longer (several minutes) execution time.

2.   SCARPEm NAPL DISCHARGE TOOL – Multi-Component NAPL

The SCARPEm solution is based on the model presented in the ER19-5223 Final Report. Dissolution of soluble components found at low mass fractions in a multicomponent NAPL can be modeled approximately by assuming the majority of the NAPL mass is inert or insoluble, i.e., the total NAPL mass and saturation are held constant. Under this assumption, the average source zone discharge concentration, C_i, and mole fraction, y_i, of NAPL component i, from a single NAPL mass, i.e., a single architectural structure, are calculated from the following equations,

$$C_i(t) = C_{i,t=0}e^{-Q_0't} + \left(\frac{K_0^*}{Q_0' - K_0'}\right)\left(e^{-K_0't} - e^{-Q_0't}\right)$$

$$y_{n,i}(t) = y_{n,i,t=0}\,e^{-K_0't}$$

where,

$$K_0' = E\frac{K_n V_{ref} C_i^*}{m_{n,total}}\left(\frac{\overline{MW_n}}{MW_i}\right)$$

$$Q_0' = \frac{1}{R_i}\left[\frac{Q_0}{\phi V_{ref}} + \left(1 - S_{n,ref}\right)\lambda_i\right]$$

$$K_0^* = E\frac{K_n C_i^* y_{n,i,t=0}}{R_i\phi}$$

The parameters making up these variables are,

K_n	=	bulk mass transfer coefficient
E	=	enhancement factor to the dissolution rate from remediation
V_{ref}	=	source zone volume containing the NAPL mass
C_i^*	=	pure phase aqueous solubility
$m_{n,total}$	=	total mass of the multicomponent NAPL
MW	=	molecular weights of component i and average for the total NAPL
R_i	=	retardation coefficient
Q	=	volumetric flow through the source zone
ϕ	=	total soil porosity
$S_{n,ref}$	=	average NAPL saturation in the source zone volume
λ_i	=	first order degradation rate constant for i
$y_{i,0}$	=	initial mole fraction of component i in the NAPL

The bulk mass transfer coefficient is based on the NAPL dissolution model derived in Stewart et al. (2022) with parameters illustrated in **Figure M.1**,

$$K_n = \frac{U_0}{V_{ref}} \left[A_{n,yz}\, \bar{k}_r + A_{n,xy} \sqrt{\frac{4}{\pi X_n}\left(\alpha_T + \frac{\phi^{1.33} D_i}{U_0}\right)} \right]$$

U_0 is the groundwater velocity, $X_S\, Y_S\, Z_S$ are the characteristic dimensions defining the source zone ($V_{ref} = X_S{*}Y_S{*}Z_S$), $X_n\, Y_n\, Z_n$ are the initial characteristic length dimensions of the soil volume containing the NAPL mass, S_n is the average NAPL saturation in the NAPL volume (assumed constant), $A_{n,xy}$ is the area for dissolution ($X_n{*}Y_n$), $A_{n,yz}$ is the vertical plane through which flow occurs ($Y_n{*}Z_n$), k_r is the average relative permeability in the NAPL volume, α_T is the vertical dispersivity and D_i is the aqueous diffusivity of component i. A diffusivity term is included but only becomes important when the groundwater velocity is very low. Methods to estimate these parameters are described in the next section.
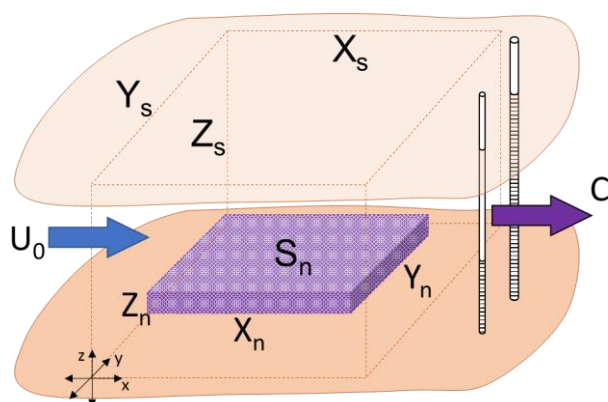
Figure M.1 –NAPL Dissolution Model Characteristic Parameters

The primary assumption in using this model is that the majority of the NAPL mass has a low solubility and that the dissolution of the soluble components does not appreciably change the total NAPL mass over the time of interest. Detailed discussion of the model can be found in the ER19-5223 Final Report. In addition, this beta version considers only a single NAPL accumulation, e.g., ganglia or pool but not both. However, the cumulative discharge from multiple masses can be manually calculated from the sum of the discharge concentrations generated by application of the model to each mass. For two masses, run the model for each mass separately using identical source zone parameters and time step; then simply add the concentrations together at each time step. Similarly, multiple soluble components can be modeled independently if all appear at low initial mass fractions in the NAPL, e.g., soluble aromatic compounds in a weathered fuel.

The tool is fully contained within an Excel spreadsheet with no need to enable macros. Double-click on the Excel file (SCARPEm_v0.1.xlsx) to open the spreadsheet. The file opens to the tab titled "Input" shown in **Figure M.2** where model parameters are entered. Details for estimating and specifying input parameters are described in the next section. Output is automatically generated in the tab named "Output" where the results can be copied and pasted into new tabs for saving and plotting. As shown in **Figure M.2**, the spreadsheet also contains tabs for estimating

technology specific dissolution enhancement factors ("Enhancement Estimator") and a tabulation of relevant properties for select chemicals ("Chemical Properties").

To perform and save output from multiple runs, new tabs can be created to save input data or the entire file can be saved and re-named (e.g., SCARPEm_v0_SiteXYZ.xlsx).
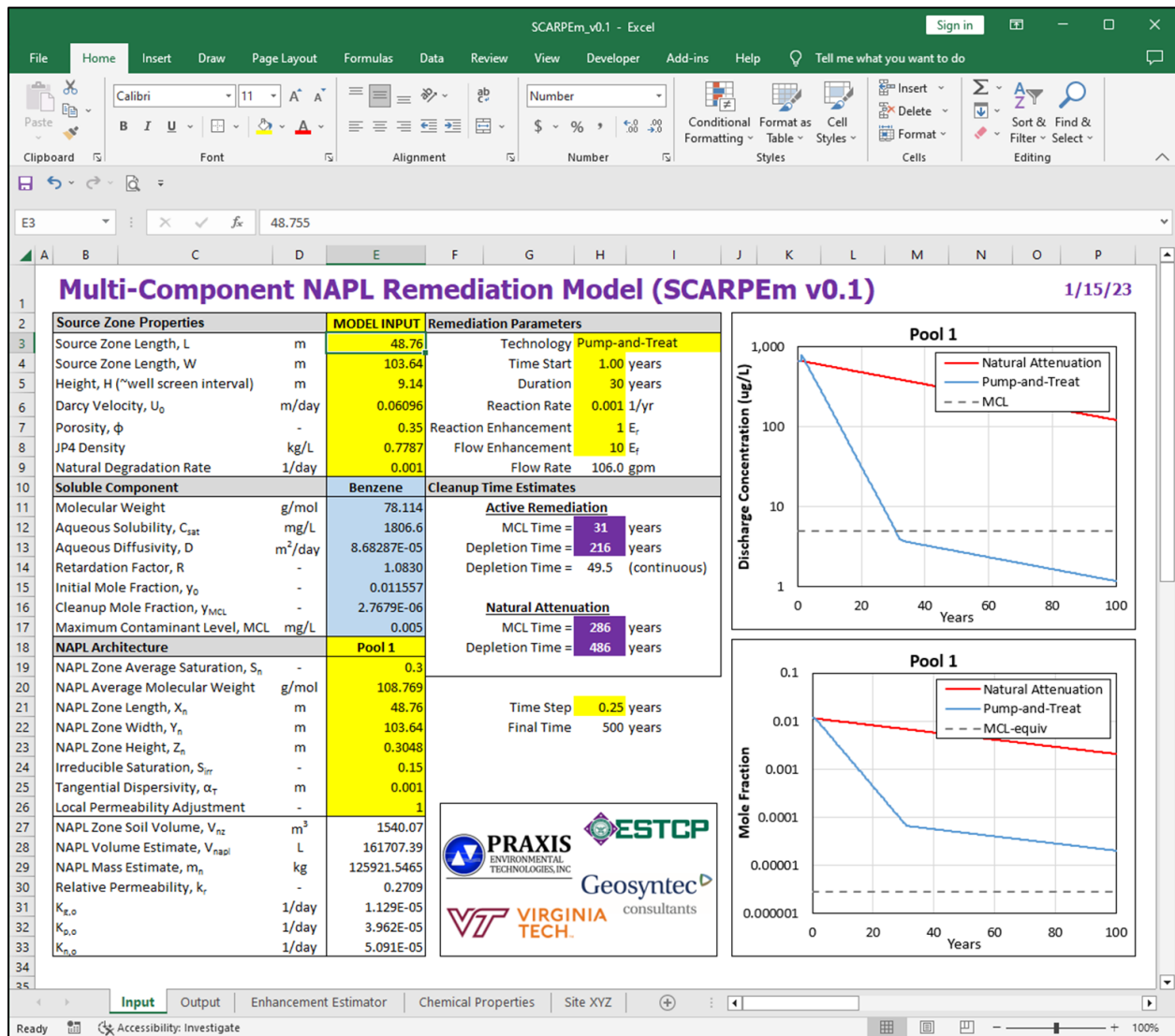

Figure M.2 – Multi-Component NAPL Model Interface

Tool Inputs

Input Parameters

Input variables are defined in five categories:

- Source Zone Properties – define the geometry and characteristics of the overall source zone

- Soluble Component Parameters – define the properties and problem-specific characteristics of the soluble component mixed in the largely insoluble NAPL.

- NAPL Architecture – define the mass, geometry and dissolution characteristics of the NAPL accumulation within the source zone (a minimum 1 mass is required)

- Remediation Parameters – define the start time and duration of a remedial activity and its enhancements through reactions (E_r) or increased flow (E_f)

- Solution Settings – define the time step for the simulation; the program automatically provides 2000 output steps yielding a total simulation time of 2000*timestep. This setting has no impact on the results although a cleanup time may not be reached if the time step is too small.

The excel file is protected and the required input variables are highlighted in yellow and light blue (see **Figure M.2**). Other calculated values with white background, e.g., total NAPL mass and the bulk mass transfer coefficient, are displayed for reference. The purple blocks represent results for calculated times of remediation based on two different metrics: a discharge concentration of MCL or depletion of the soluble component from the NAPL to a cleanup-level equivalent, i.e., diminishing the mole fraction in the NAPL to a value representing equilibrium with water at the cleanup concentration.

Methods to obtain or estimate the required input parameters are described in **Table S.1** accompanying the single component NAPL model. The only additional required input is the initial mole fraction of the soluble component in the NAPL. This parameter can be estimated from analyses of NAPL samples and an estimate of the NAPL makeup is generally available at sites with multi-component NAPL as this information is fundamental to any activities at the site.

Estimates for remedial impacts can be generated with technology-specific reaction rates and associated changes in flow to enhance NAPL dissolution. The potential enhancement is relative to the natural gradient for flow and the NAPL architecture. For example, when groundwater pumping is performed the characteristic velocity through the source zone increases and the ratio to the natural flow provides the enhancement factor. More robust methods for estimating the enhancement factor are described in the next section. The equations are programmed into the tab "Enhancement Estimator" as illustrated in **Figure M.3**.

For first order processes typical of biological degradation, the only required parameter is an estimate for the reaction rate constant. The other parameters are linked to values in the input tab.

However, the calculated reactive enhancement factor is not linked back to the input tab and the user is required to manually transfer the enhancement factor. The theoretical calculations for enhancement are considered guidance rather definitive results. Numerous methods are available in the literature for determining the first order rate constant from field and laboratory data. Most sites with appreciable biological degradation should have an estimate for site-specific values. The second order reaction rate enhancement factor is described in the next section. Details on estimating flow enhancements and reactive enhancements along with example applications can be found in the Final Report for ER19-5223 available at ER19-5223 Project Overview (serdp-estcp.org).

Figure M.3 – Enhancement Factor Estimation Tool

Tool Outputs

The output consists of 2000 timesteps with the total simulation time equal to 2000*timestep. The timestep setting has no impact on the results although a cleanup time may not be reached if the time step is too small. Assuming the duration is sufficient to attain the cleanup goal, the time to attain an average discharge concentration less than MCL is displayed in the Input tab in the purple-shaded box labelled, "MCL Time". Note, the characteristic dimensions of the source zone, particularly the vertical interval, are akin to specifying dilution in accordance with the measurement scale, e.g., the screen interval of a groundwater monitoring well. The time required to deplete the soluble component to a mole fraction in the NAPL equivalent to an MCL equilibrium is displayed in the purple-shaded box labeled, "Depletion Time." The depletion time is independent of the source zone dimensions, i.e., no dilution occurs, and the time represents a very stringent cleanup goal.

The transient results of the calculation are automatically written to the tab "Output". The data are the discharge concentration and mole fraction of soluble component remaining in the NAPL mass as a function of time with no remedial efforts (Natural Attenuation) and the corresponding data for the remedial process considered. The user can provide any desired name for the remedial process. Example output is illustrated in a screen shot from the Output tab in **Figure M.4** for a pump-and-treat application.

Figure M.4 – Example Results for the "Output" Tab

3. THEORETICAL NAPL DISSOLUTION ENHANCEMENT FACTORS

Remedial enhancements to NAPL dissolution can be grouped into three categories: increases in flow (E_f), reactive increases in driving concentration gradients (E_r), and increases in effective solubility (E_s). This section describes theoretical enhancements available in the literature for flow and reactive enhancements used in the modeling. Solubility enhancements are not considered here but are available in the literature as a function of the injected chemical agent concentration (e.g., Wang and Brusseau 1993, McCray et al. 2000, Saba et al. 2002, Suchomel et al. 2007, Demiray et al. 2021).

Flow Enhancement

Changing the characteristic velocity through the NAPL-impacted volume is expected to yield a roughly linear change to dissolution rates for cases of practical interest, e.g., pump-and-treat. The flow enhancement factor (E_f) is defined as,

$$E_f = \frac{U_{remedy}}{U_0}$$

The increased flow increases the dissolution rate but also reduces the residence time and therefore decreases an associated reactive enhancement attributable to natural processes.

Reactive Enhancement

Reactive dissolution enhancements result from increased driving concentration gradients. However, the enhancement is not a simple linear function of the reaction rate but also depends strongly on the advection rate, U_0, the length of the NAPL zone, X_n., i.e., the source zone residence time, the concentration of reactants, and the reaction rate. The discharge concentration of a soluble component i from the reference soil volume under generic reactive conditions is represented by,

$$R_i \frac{dC_i}{dt} = -\frac{Q_0}{\phi V_{ref}} C_i - \frac{1}{\phi V_{ref}} \frac{dm_{n,i}}{dt} - \left(1 - S_{n,ref}\right) r_i$$

r_i is the reaction sink for the contaminant. Reactions are generally described as a first order process when the reactant is provided in excess, the aqueous contaminant is limited, and rates are slow to moderate. The reaction can be characterized as second order between the reactant and aqueous contaminant when reaction rates are fast such that the injected reactant is also limited. The reaction term in for each case is defined by,

$$1st\ Order:\ r_{i,1} = \lambda_i C_i \qquad 2nd\ Order:\ r_{i,2} = \kappa_{i,react} C_{react} C_i$$

λ_i is a first order decay constant, C_{react} represents the concentration of introduced reactant, and $\kappa_{i,react}$ is the specific reaction rate coefficient. The most common condition for modeling reactions associated with NAPL dissolution is first order because most studies address biological

enhancements which are relatively slow. However, fast reactions observed during in situ chemical oxidation can yield a second order process.

Dimensionless Parameters for Characterizing First Order Enhancements

Theoretical enhancement factors under first order reactive conditions have been derived by Seagren et al. (1994) and Christ and Abriola (2007) for idealized NAPL pool and ganglia architectures, respectively. Discussion of these and other theoretical relationships can be found in Seagren and Becker (2015). The relationships are written in terms of dimensionless parameters describing the relative rates of differing processes associated with the flow and NAPL architecture. The ratio of the characteristic reaction rate to the advection rate of water through the NAPL-impacted soil volume is known as the reaction-based Damköhler Number, *Da*. The Stanton Number, *St*, is the ratio of the mass dissolution rate to the advection rate. The Peclet number, *Pe*, is the ratio of the advection rate to the longitudinal dispersion rate; however, on the scale of typical NAPL source zones in the field, the Peclet number is expected to be large. *Da*, *St* and *Pe* are defined as follows, assuming a first order reaction,

$$Da = \frac{\lambda_r X_n \phi}{U_0} \qquad St = \frac{K_n X_n}{\phi U_0} \qquad Pe = \frac{U_0 X_n}{D_x \phi} = \frac{X_n}{\alpha_L}$$

α_L is the longitudinal hydrodynamic dispersivity. Substituting the upscaled mass transfer coefficient (Eqn 4 from the main text) into the Stanton number yields an upscaled Stanton number,

$$St = \frac{1}{\phi} \left[\bar{k}_r + \frac{2}{Z_n} \sqrt{\frac{X_n}{\pi} \left(\alpha_T + \frac{\phi^{1.33} D_i}{U_0} \right)} \right]$$

Inspection of the upscaled Stanton number with field-scale parameters indicates *St* is on the order of the inverse porosity or smaller. For ganglia, the relative permeability approaches one and the dispersivity term is small. For pools, with high saturations, the relative permeability may approach zero while the dispersivity term is expected to be <1 on the field scale. The longitudinal, hydrodynamic dispersivity is generally on the order of 0.1-1 m (Molz 2015) and therefore the field-scale Peclet number is expected to be greater than one.

Theoretical Dissolution Enhancements with First Order Reactions

Seagren et al. (1994) derived a theoretical expression for the reaction enhancement to NAPL dissolution during flow over a NAPL pool with a first order reaction in the aqueous phase under pseudo-steady conditions. The model neglects any flow through the NAPL zone and is solely a function of the Damköhler number,

$$E_{r,p} = \frac{1}{2}\sqrt{\frac{\pi}{Da}}\left[\left(Da + \frac{1}{2}\right)erf(\sqrt{Da}) + \sqrt{\frac{Da}{\pi}}\,exp(-Da)\right]$$

To induce an enhancement factor of 2 or larger, *Da* must be 4 or larger.

Christ and Abriola (2007) derived an expression for first order reaction enhancement to NAPL dissolution during flow through ganglia, also under pseudo-steady conditions. In this architecture, the reaction enhancement is also a function of the Stanton and Peclet numbers,

$$E_{r,g} = \frac{St - \left(\frac{St}{St + Da}\right)^2\left(St + Da - \left\{1 - exp\left[\frac{Pe}{2}\left(1 - \sqrt{1 + \frac{4(St + Da)}{Pe}}\right)\right]\right\}\right)}{1 - exp\left[\frac{Pe}{2}\left(1 - \sqrt{1 + \frac{4St}{Pe}}\right)\right]}$$

The enhancement for ganglia increases with increasing *St*, decreasing *Pe*, and increasing *Da*. For a maximum *St* of 3, i.e., inverse porosity, and a minimum Pe of 1, a minimum *Da* value of 2 or larger is required to induce an enhancement factor of 2 or more. However, for the vast majority of field applications, *Pe* for NAPL dissolution will be large and first order reactive enhancements will only be appreciable if *St* is large, i.e., >10. NAPL dissolution is a relatively long process compared to a relatively short residence time; therefore, *St* is usually small. Hence, typical first order reactions are not expected to enhance ganglia dissolution where the interfacial area between water and NAPL is large as compared to pools with limited interfacial area.

Noting the theoretical enhancement factors were derived for two idealized architectures, an appropriate application of first order reaction enhancements in the upscaled dissolution model takes the form,

$$E_{r,1}K_{n,0} = E_{r,g}K_{g,0} + E_{r,p}K_{p,0}$$

$$E_{r,1}K_{n,0} = \frac{U_0}{V_n}\left[E_{r,g}A_{n,yz}\,\bar{k}_r + E_{r,p}A_{n,xy}\sqrt{\frac{4}{\pi X_n}\left(\alpha_T + \frac{\phi^{1.33}D_i}{U_0}\right)}\right]$$

More complex relationships specific to biological degradation assuming Monod kinetics can be found in Phelan et al. (2015).

Theoretical Dissolution Enhancements with Second Order Reactions

Second order reactions can be characterized by fast reaction rates, resulting in limited reactant availability in the vicinity of the dissolving NAPL mass. The fast rate results in a deficit of both the reactant and contaminant at a reaction front distant but close to the NAPL-water interface. The result is a steep increase in the driving concentration gradient for mass dissolution. First

order reactions described above assume the reaction rate is slow enough for the excess reactant and contaminant to co-exist and mingle for some time in the vicinity of the NAPL mass. Cussler (1992) derived a theoretical expression for these second order conditions based primarily on the ratio of bulk concentration of reactant to the cumulative effective solubilities of the NAPL components. Cussler's approach assumes the rate of aqueous diffusion and dispersion is too slow to keep up with reactions and his derived pure-component enhancement factor is modified for a multi-component NAPL as,

$$E_{r,2} = 1 + \frac{1}{Y_{react}}\left(\frac{C_{react}}{\sum y_i C_i^*}\right)\left(\frac{D_i}{D_{react}}\right)$$

Y_{react} is the stoichiometric molar mass ratio for the reaction of reactant with soluble NAPL components. The assumptions underlying this expression include a steady re-supply of the reactant to maintain a constant bulk concentration, reactions of multiple soluble components occur independently, and dissolved contaminants are completely destroyed at a reaction interface. The summation of soluble components in the denominator accounts for multiple NAPL components contributing to the depletion of the reactant. The ratio of aqueous phase diffusion coefficients provides a small correction for differences in diffusion rates between the soluble component and reacting amendment. The modification for a multi-component NAPL includes the complexity of a transient, depleting mole fraction. In this work, a constant enhancement is conservatively assumed based on the initial mole fraction because, as the mole fraction approaches zero, the enhancement unrealistically approaches infinity while other NAPL components may continue to deplete the reactant.

The Final Report for ER19-5223 contains a detailed example in Appendix E for calculating the second order enhancement factor of a multi-component NAPL in the presence of an oxidant. Consider a typical fuel hydrocarbon which includes multiple aromatics such as benzene, toluene, xylenes, and naphthalene compounds. The aromatic compounds as a group typically make up the vast majority of appreciably soluble components in a weathered NAPL and generally appear at a low fraction of the total, e.g., 10% to 20%. As such, each component is assumed to deplete independently; however, each component reacts and depletes the oxidant. Hence, the second order enhancement equation includes two terms in the denominator that are averages for the aromatic group: the stoichiometric molar mass ratio (Y_{react}) and the total effective solubility of the NAPL ($\sum y_i C_i^*$). As described in the example, representative values for weathered JP-4 are a molar ratio of about 18 and an initial total effective solubility of about 40 mg/L. The example provides the methodology for estimating these parameters for other multi-component NAPL mixtures.

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