R-UNSAT

DOCUMENTATION OF R-UNSAT, A COMPUTER MODEL FOR THE SIMULATION OF REACTIVE, MULTISPECIES TRANSPORT IN THE UNSATURATED ZONE

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Graphical interface development funded by NJ DEP - DSR

TABLE OF CONTENTS

The Windows Interface

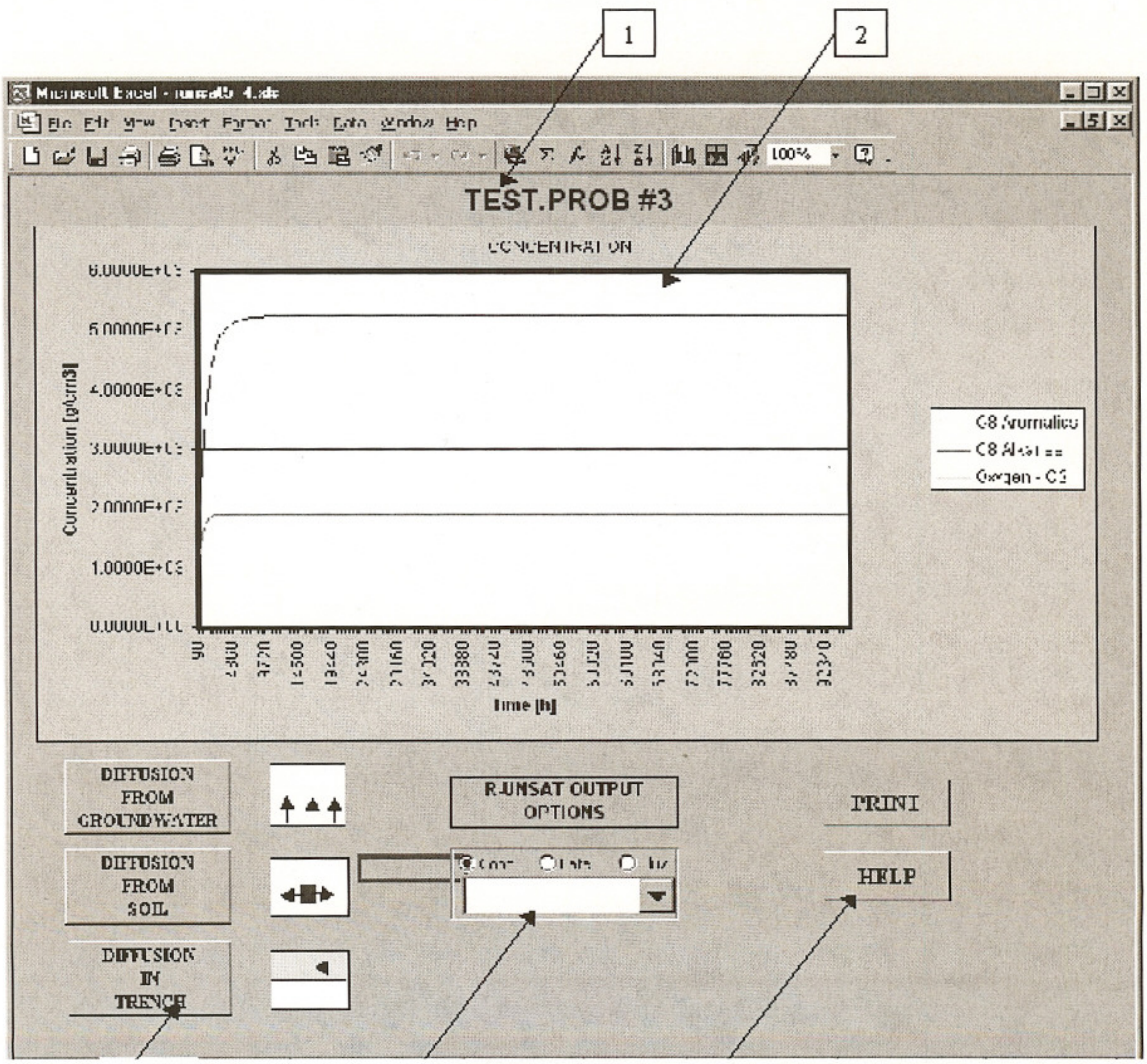
THE WINDOWS INTERFACE

1 The Main Screen

The Windows interface is a Microsoft Excel application consisted from the main screen, data entry forms and extensive Visual Basic code.

The main screen (see figure 33) has the following components:

- The model title (item 1)
- The results presentation area (item 2)
- The results selection control (item 3)
- The command buttons (items 4):
  - DIFFUSION FROM GROUNDWATER
  - DIFFUSION FROM SOIL
  - DIFFUSION IN TRENCH
  - PRINT
  - HELP



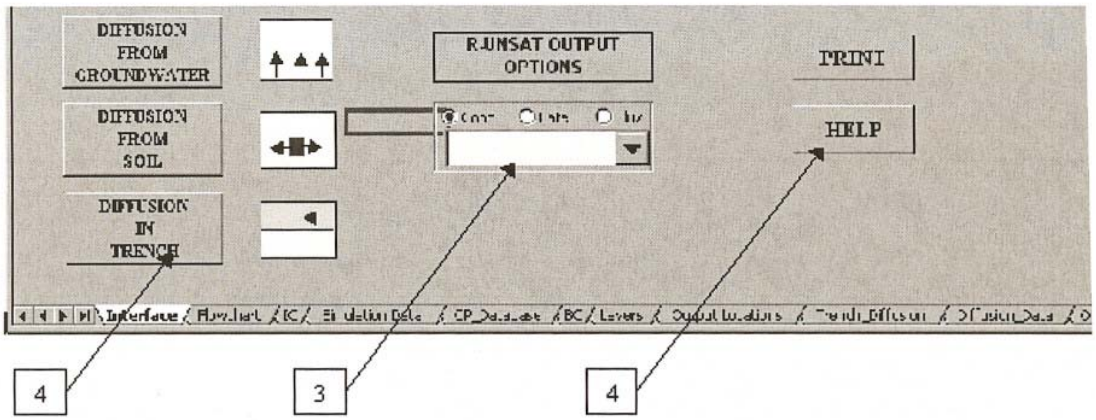


Figure 33. Windows interface main screen

Followed by 2 - Running Soil Diffusion Model or 3 - Running Diffusion in Trench Model

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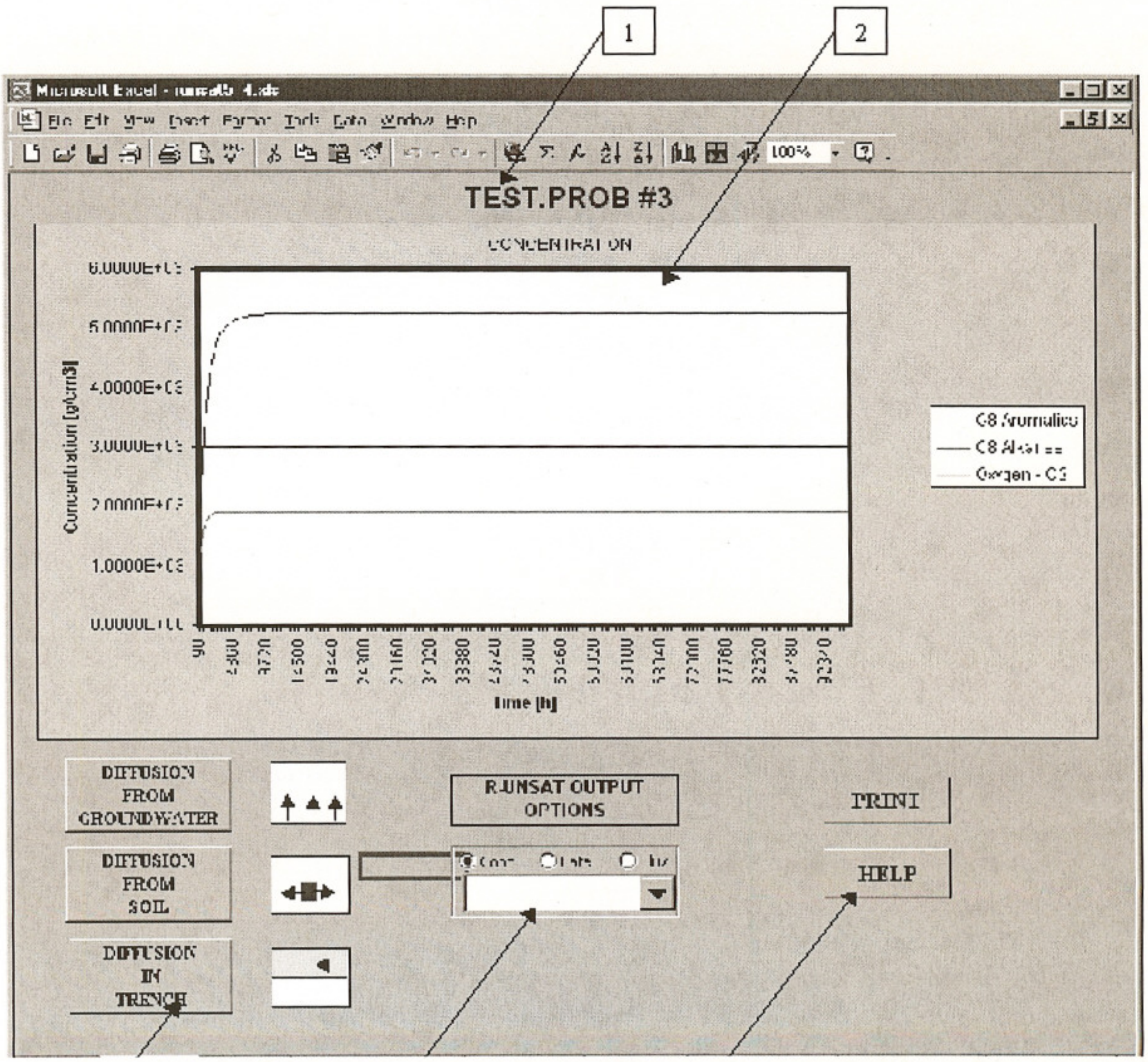


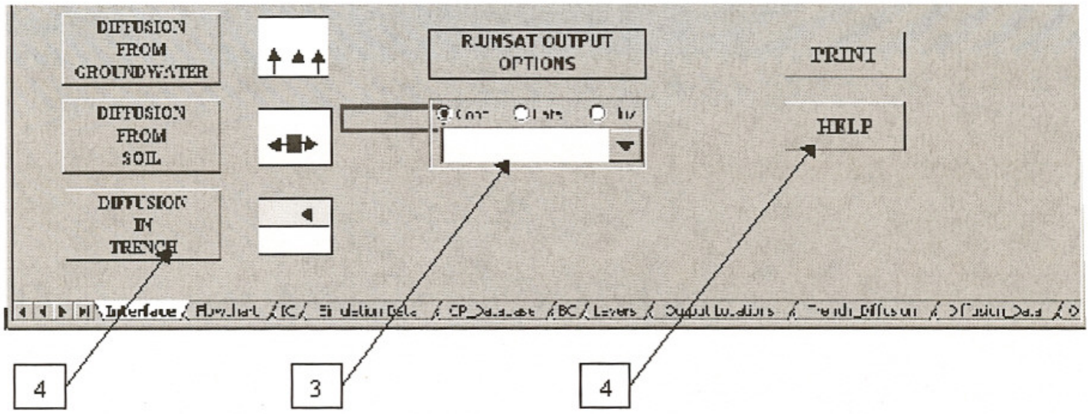


Figure 33. Windows interface main screen

Followed by 2 - Running Soil Diffusion Model or 3 - Running Diffusion in Trench Model

THE WINDOWS INTERFACE

2 Running Soil Diffusion Model

Before running either an existing or a new model the user has to set the model options.
Press DIFFUSION FROM GROUNDWATER or DIFFUSION FROM SOIL buttons. They will diplay the following dialogs:

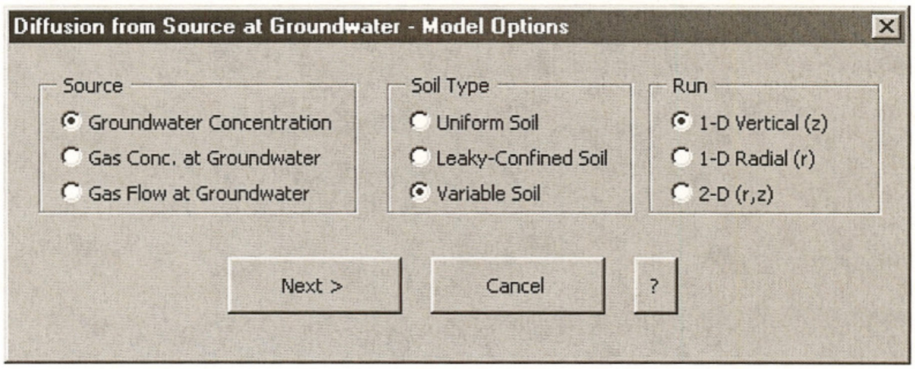


Figure 34a. Diffusion from Source at Groundwater model options dialog

If "Uniform Soil" or "Leaky-Confined Soil" options are selected an analitycal model run is assumed. In this case tl run options are disabled. "Variable Soil" option assumes a numerical model run and rhe run options are enabled fc user selections.

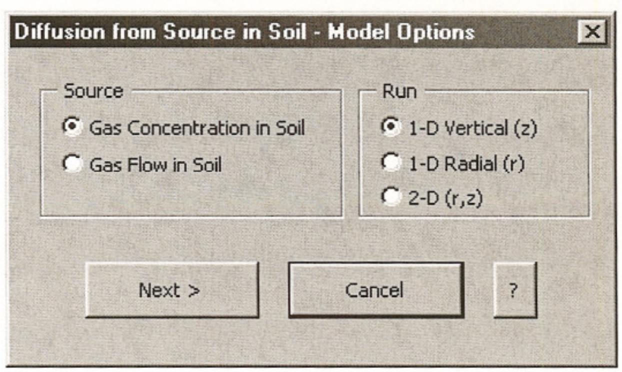


Figure 34b. Diffusion from Source in Soil model options dialog

Diffusion from Source in Soil always assumes a numerical model run.

Once the user chooses the model options, the data entry wizard is launched with the Step 1 form:

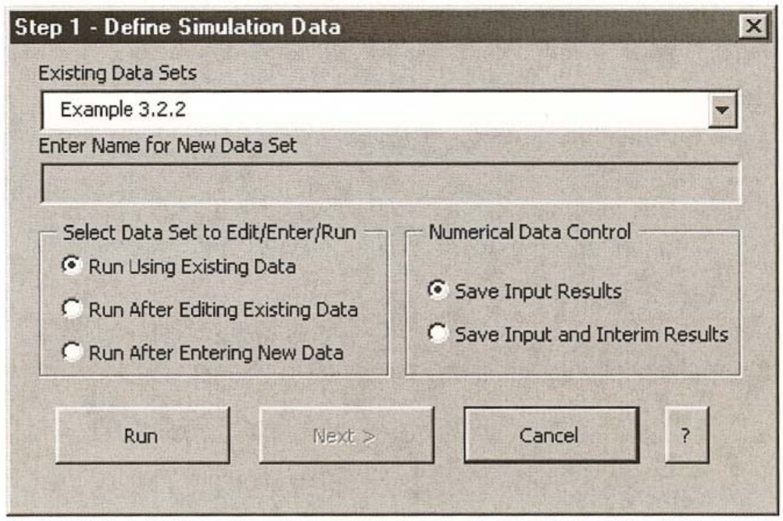


Figure 34c. Step 1 - Define Simulation Data

The user has to check one of the "Data Set Edit/View" options. The choice affects the "Previous Input Data" and "New Simulation ID" as follows:

- "Run Using Existing File" activates only the "Previous Input Data" field. The user can select fron this drop-down box a previous defined dataset for the current run;
- "Run After Editing File" activates both "Previous Input Data" and "New Simulation ID" allowing the user to modify an existing data set and optionally to save the modified dataset under a new ID;
- "Run Using New File" option activates only the "New Simulation ID" allowing user to define a new dataset from scratch.

The next steps of the data entry procedure depend on the chosen analysis method.

Followed by 2.1 - Entering Soil Diffusion Input Data (Analytical) or
2.2 - Entering Soil Diffusion Input Data (Numerical)

Entering Model Input Data (Analytical)

THE WINDOWS INTERFACE

2 Running Soil Diffusion Model

2.1 Entering Soil Diffusion Input Data (Analytical)

The analytical method passes over the following steps:

- Step 2 - Boundary and Initial Conditions (figure 35);
- Constituent Properties (figure 36), if the "Initial Condition Option is set to "Input File";
- Step 3 - Physical Properties of the Constituent (figure 37);
- Step 4 - Lithologic Properties (figure 38), and
- Step 5 - Output Parameters (figure 39).

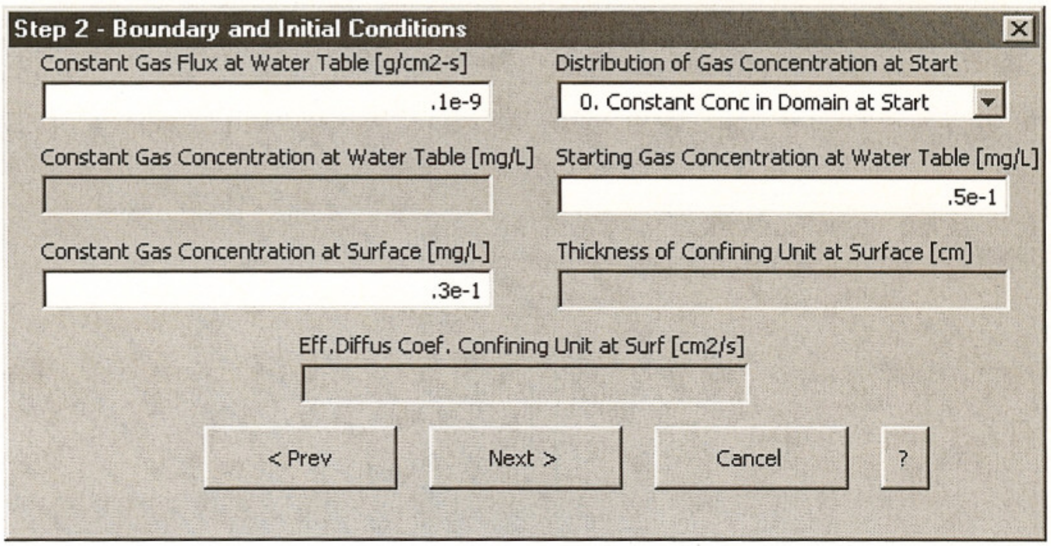


Figure 35. Step 2- Boundary and Initial Conditions

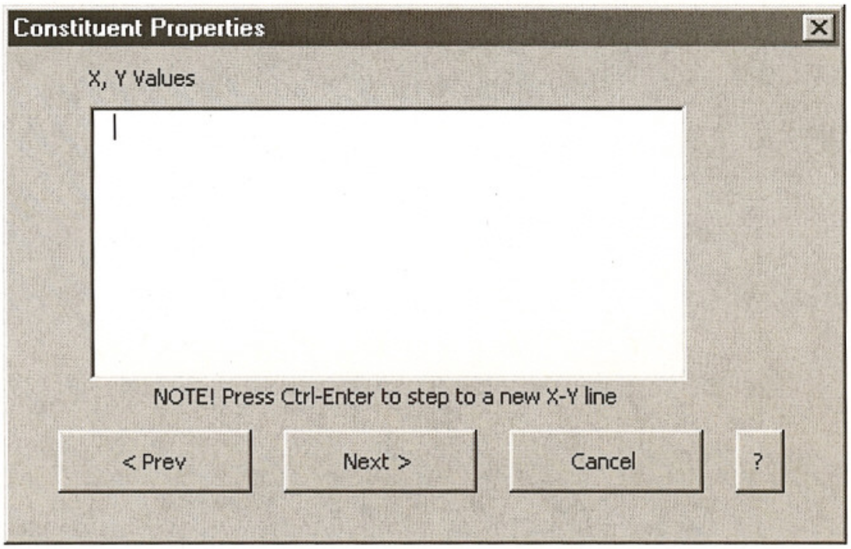


Figure 36. Constituent Properties

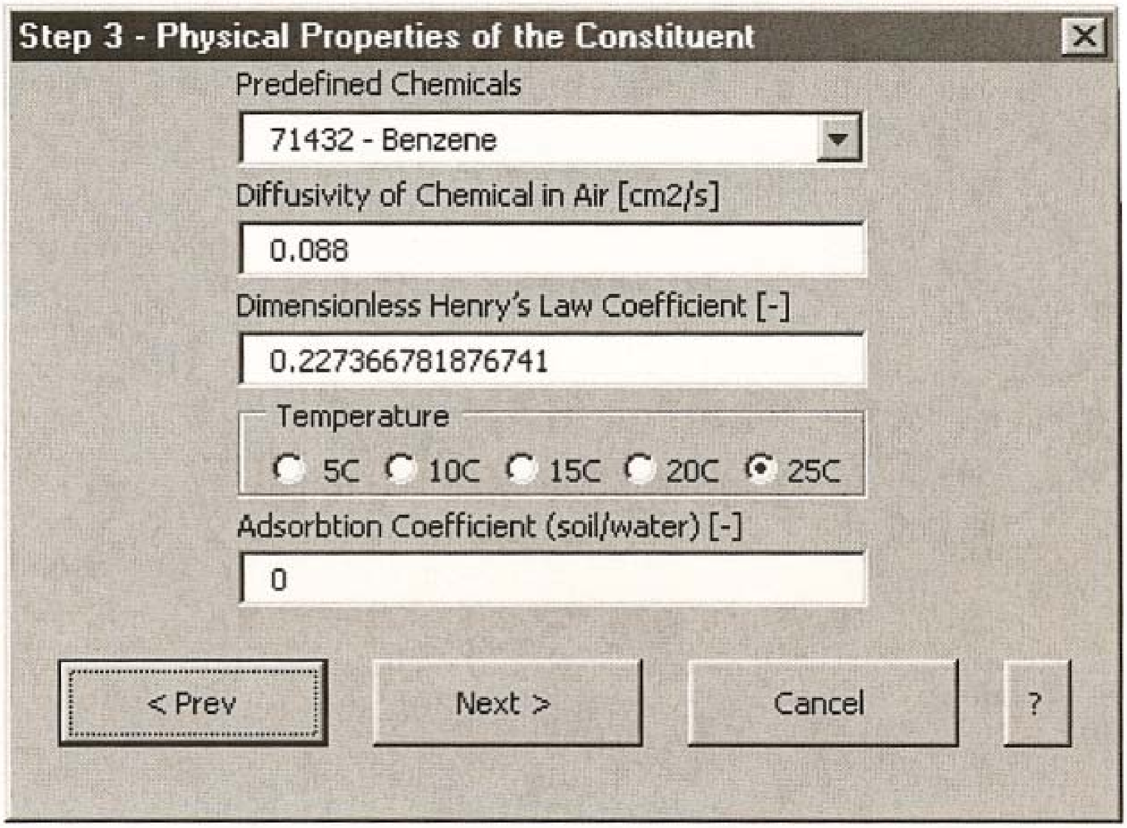


Figure 37. Step 3- Physical Properties of the Constituent

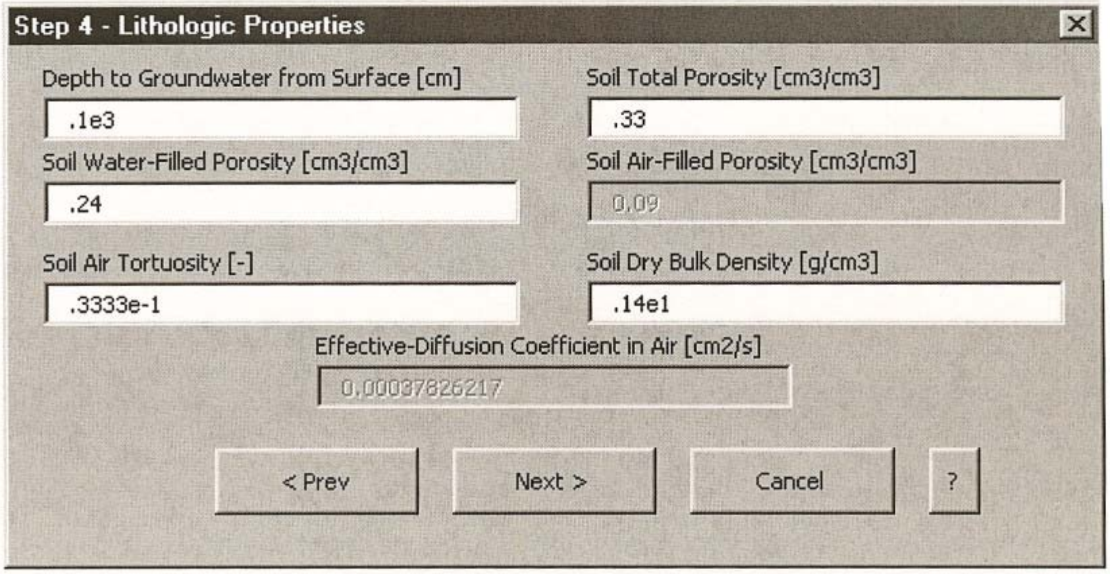


Figure 38. Step 4 – Lithologic Properties

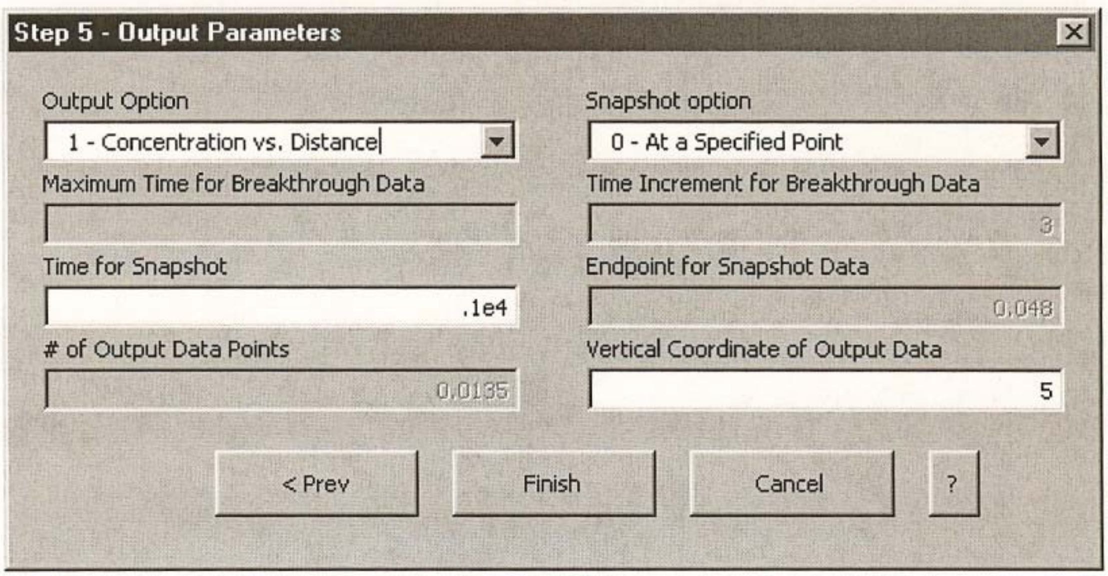


Figure 39. Step 5 – Output Parameter

Followed by 2.2 - Entering Soil Diffusion Input Data (Numerical)

Entering Model Input Data (Vapor Diffusion)

THE WINDOWS INTERFACE

3 Running Diffusion In Trench Model

The vapor diffusion calculation passes over the following steps:

- Step 1 – Flow Domain Geometry (figure 50);
- Step 2 – Chemical type (figure 51);
- Step 3 – Diffusion properties (figure 52);
- Step 4 – Advection properties (figure 53);
- Step 5 – Decay parameters (figure 54).

The results of the diffusion in trench model are displayed in a tabular format as presented in figure 55. The model parameters are entered using the folowing dialog forms:

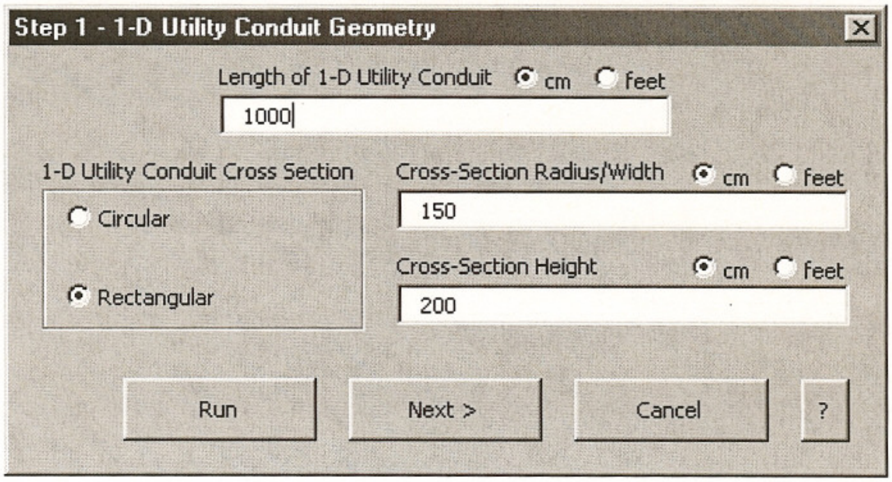


Figure 50. Step 1 – Flow Domain Geometry

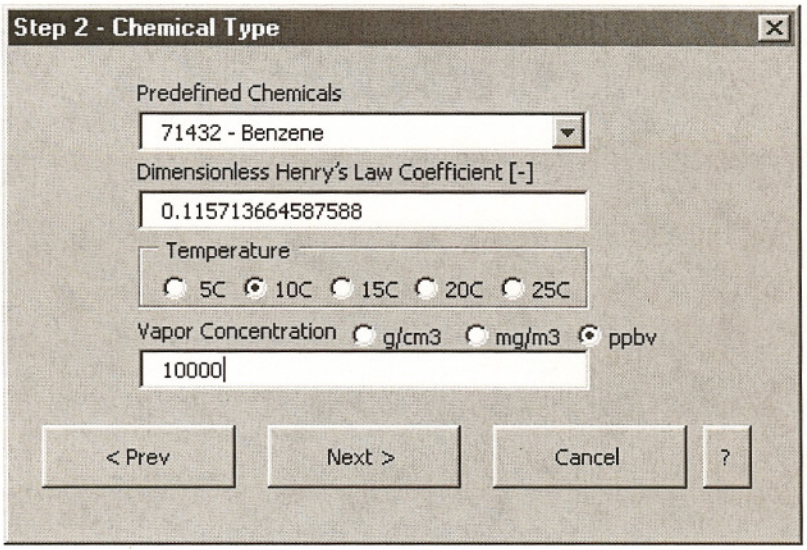


Figure 51. Step 2 – Chemical type

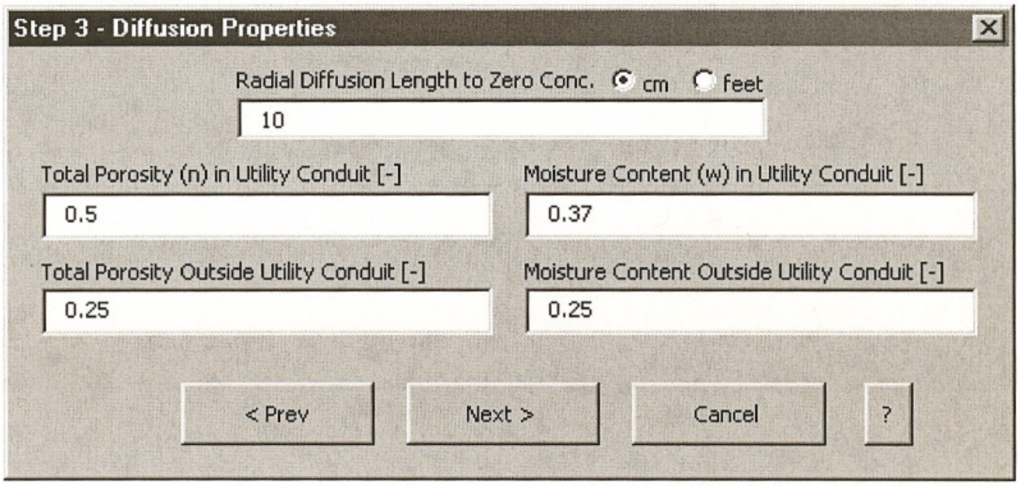


Figure 52. Step 3 – Diffusion properties

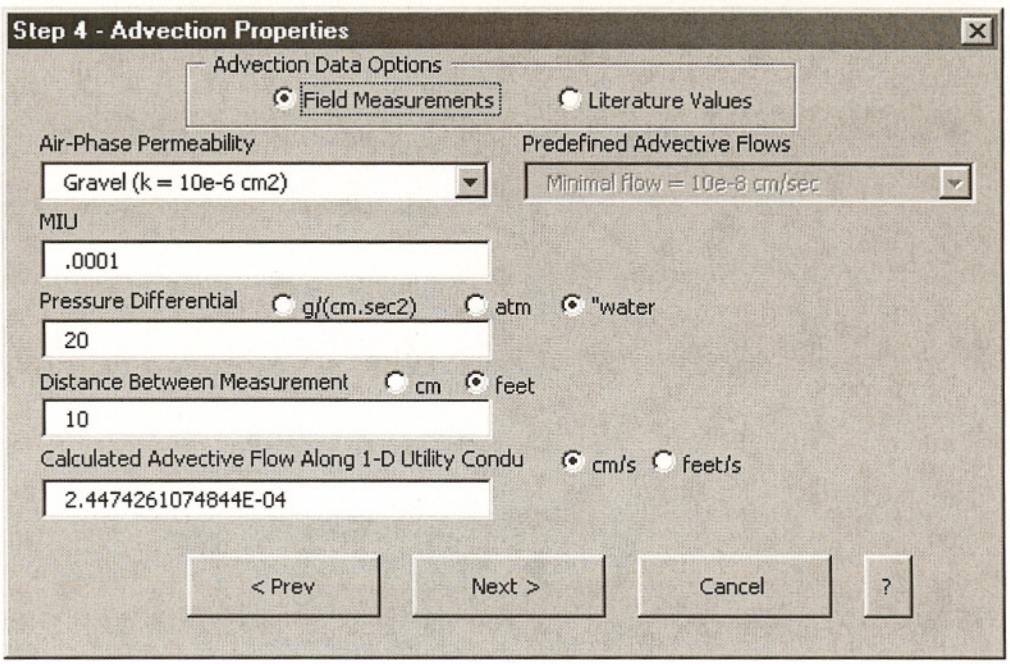


Figure 53. Step 4 – Advection properties

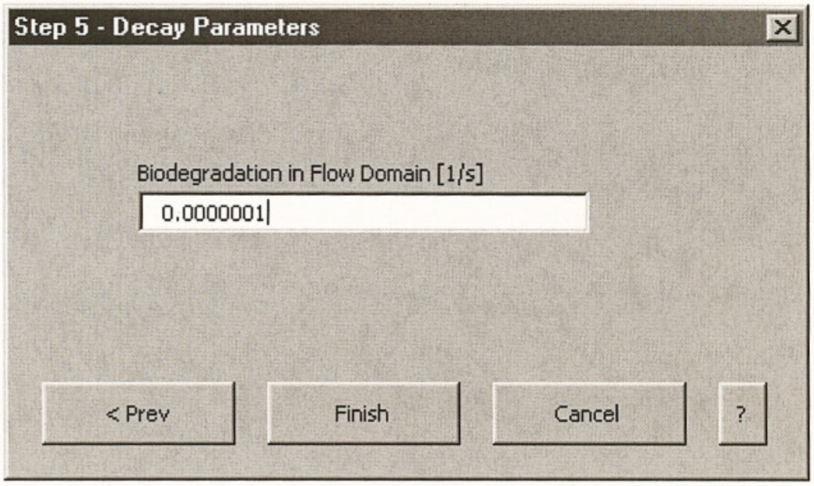
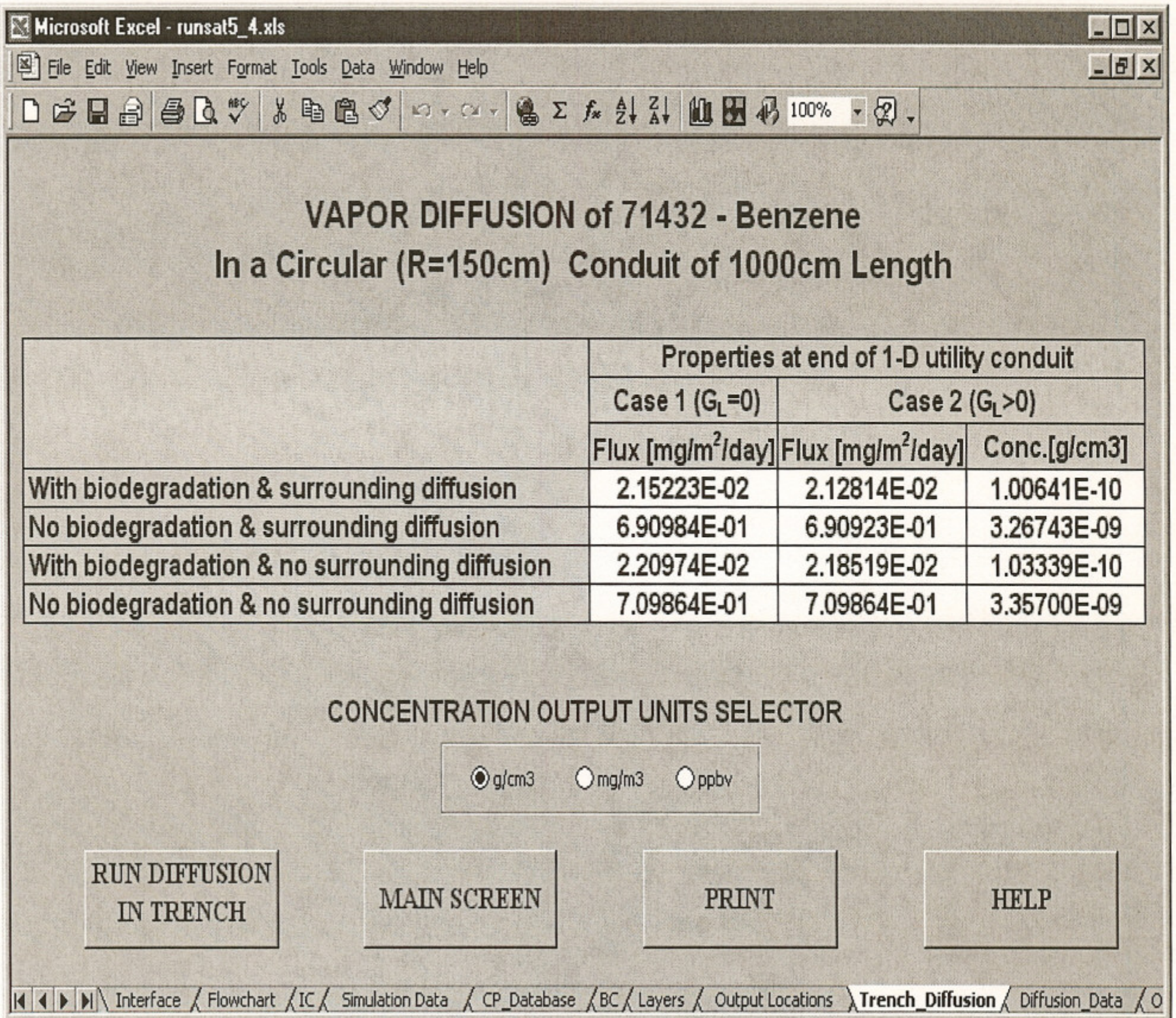


Figure 54. Step 5 – Decay parameters



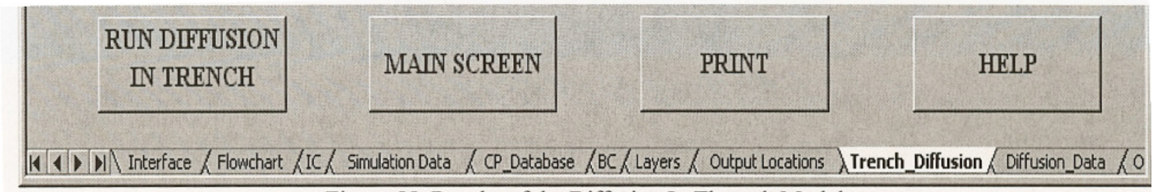


Figure 55. Results of the Diffusion In Thrench Model

Tipical Values for Input Parameters

TYPICAL VALUES FOR INPUT PARAMETERS

Typical Values for Porosity

Gravel High n = 0.40
Gravel Medium n = 0.33
Gravel Low n = 0.25
Sand High n = 0.50
Sand Medium n = 0.37
Sand Low n = 0.25
Silt High n = 0.50
Silt Medium n = 0.43
Silt Low n = 0.35
Clay High n = 0.70
Clay Medium n = 0.55
Clay Low n = 0.40

Typical Values for Moisture Content

Gravel = .25
Sand = .25
Silt = .35
Clay = .40

Typical Values for Air Phase Permeability

Fine sand k = 10e-9 cm2
Medium sand k = 10e-8 cm2
Coarse sand (k = 10e-7 cm2
Gravel k = 10e-6 cm2

Typical Values for Air Flow

Very high flow = 10e-4 cm/sec
High flow = 10e-5 cm/sec
Moderate flow = 10e-6 cm/sec
Low flow = 10e-7 cm/sec
Minimal flow = 10e-8 cm/sec

Typical Values for Decay (1/sec)

No degradation = 0 /sec
Degradation for MTBE = 0.00000001 /ses
Low degradation for BTEX = 0.0000001 /sec

Moderate degradation for BTEX = 0.000001 /sec
High degradation for BTEX = 0.00001 /sec

Analytical Solutions for 1-D Movement in a Leaking Trench

ANALYTICAL SOLUTIONS FOR 1-D MOVEMENT IN A LEAKING TRENCH

1. Governing Equation

$$s\frac{\partial G}{\partial t} = D\frac{\partial^2 G}{\partial z^2} - q\frac{\partial G}{\partial z} - R$$

where,

G = concentration in gas phase [g/cm^3]

$s = \theta_a + \frac{\theta_w}{H} + \frac{K\rho_b}{H}$	Equilibrium partitioning
$D \equiv D_a$	Diffusion only in gas phase considered
q	Advection only in air phase considered for conduit
R	Losses due to degradation and diffusive loss through conduit walls

Assume a, D, q_a are constant in equation derivation.

$$R = \frac{\lambda_B}{H}G + \lambda_D G \equiv \lambda G \qquad \text{where } \lambda = \left(\frac{\lambda_B}{H} + \lambda_D\right)$$

Assume first order biological decay characterized by λ_B for aqueous phase degradation.
λ_D Characterizes wall geometry and conduit/surroundings interface.

Characterize λ_D for diffusive loss to surrounding medium continuity at interface

$\lambda_D G$ loss per unit volume (inside out)

$$\Delta V \lambda_D G = J_1 dS = J_2 dS$$

$\Delta V = \Delta z A$ — A = Cross-sectional area of conduit

$dS = \delta \Delta z$ — δ = Circumference of conduit

$$\lambda_D G = J_2 \frac{\delta}{A}$$

$J_2 = D_s \frac{G - O}{L_s}$ — D_s Diffusion coefficient for surrounding medium

$\lambda_D G = \frac{D_s G}{L_s} \frac{\delta}{A}$ — L_s Characteristic length for concentrations to drop to zero in surrounding medium

$$\lambda_D = \frac{D_s}{L_s} \frac{\delta}{A}$$

If conduit is a cylinder $\frac{\delta}{A} = \frac{2\pi r}{\pi r^2} = \frac{2}{r}$

If conduit is a box $\frac{\delta}{A} = \frac{2(a+b)}{ab} = 2\left(\frac{1}{b} + \frac{1}{a}\right)$

The basic governing equation then is:

$$s \frac{\partial G}{2t} = D \frac{\partial^2 G}{2z^2} - q \frac{\partial G}{2z} - \lambda G$$

2. <u>Steady State Solutions</u>

Let $x = \frac{z}{L}$ where L is the length of conduit from source to structure

$$\frac{d^2G}{dx^2} - P_e \frac{dG}{dx} - B_a G = 0$$

Peclet $P_e = \frac{qL}{D}$ Domkooler $B_a = \frac{\lambda L^2}{D}$

$r^2 - P_e r - B_a G = 0$ Characteristic equation

$$r = \frac{P_e \pm \sqrt{P_e^2 + 4B_a}}{2} \qquad r_1 = \frac{P_e}{2} + \left(\frac{P_e^2}{4} + B_a\right)^{1/2} \qquad r_2 = \frac{P_e}{2} + \left(\frac{P_e^2}{4} + B_a\right)^{1/}$$

$G = A_1 e^{r_1 x} + B_1 e^{r_2 x}$ General solution

Flux $J = qG - D\frac{dG}{dz} = qG - \frac{D}{L}\frac{dG}{dx}$

$$\frac{dG}{dx} = r_1 A_1 e^{r_1 x} + r_2 B_1 e^{r_2 x}$$

Case 1: Maximal Transport into Structure (Diffusion maximal)

$x = 0 \qquad G = G_0$ Source concentration (at equilibration with product

$x = 1 \qquad G = 0$ Maximal transport at basement

$$A_1 + B_1 = G_0$$

$$A_1 e^{\gamma_1} + B_1 e^{\gamma_2} = 0$$

$$A_1 = \frac{\begin{vmatrix} G_0 & 1 \\ 0 & e^{\gamma_2} \end{vmatrix}}{\begin{vmatrix} 1 & 1 \\ e^{\gamma_1} & e^{\gamma_2} \end{vmatrix}} = \frac{G_0 e^{\gamma_2}}{e^{\gamma_2} - e^{\gamma_1}}$$

$$A_1 = \frac{\begin{vmatrix} 1 & G_0 \\ e^{\gamma_1} & 0 \end{vmatrix}}{\begin{vmatrix} 1 & 1 \\ e^{\gamma_1} & e^{\gamma_2} \end{vmatrix}} = \frac{-G_0 e^{\gamma_1}}{e^{\gamma_2} - e^{\gamma_1}}$$

$$\frac{G}{G_0} = \frac{1}{e^{\gamma_2} - e^{\gamma_1}} \left\{ e^{\gamma_2} e^{\gamma_1 x} - e^{\gamma_1} e^{\gamma_2 x} \right\}$$

Flux

$$\frac{dG}{dx} = \frac{G_0}{e^{r_2} - e^{r_1}} \left\{ r_1 e^{r_1} e^{r_2 x} \right\}$$

For the case of diffusion only, $J = \frac{-D}{L} \frac{dG}{dx}$

In general,

$$\frac{J}{qG_0} = \frac{qG}{qG_0} - \frac{D}{LqG_0} \frac{dG}{dx} = \frac{G}{G_0} - \frac{1}{P_e} \frac{1}{e^{r_2} - e^{r_1}} \left\{ r_1 e^{r_2} e^{r_1 x} - r_2 e^{r_1} e^{r_2 x} \right.$$

Concentration at $x = 1$ $G = 0$ for this case

Flux at $x = 1$

$$\frac{J}{qG_0} = -\frac{1}{P_e} \frac{1}{e^{r_2} - e^{r_1}} \left\{ r_1 e^{r_2} e^{r_1} - r_2 e^{r_1} e^{r_2} \right\}$$

$$e^{r_1} e^{r_2} = e^{r_1 + r_2} = \exp(P_e)$$

$$\frac{J}{qG_0} = -\frac{1}{P_e} \left[\frac{\exp(P_e)}{\exp(r^2) - \exp(r^1)} \right] (r_1 - r_2)$$

Case 2: <u>Diffusion Minimal</u>

For boundary conditions:

$$x = 0 \qquad G = G_0$$

$$x = 1 \qquad \frac{dG}{dx} = 0$$

$$A_1 + B_1 = G_0$$

$$r_1 A_1 e^{r_1} + r_2 B_1 e^{r_2} = 0$$

$$A_1 = \frac{\begin{vmatrix} G_0 & 1 \\ 0 & r_2 e^{r_2} \end{vmatrix}}{\begin{vmatrix} 1 & 1 \\ r_1 e^{r_1} & r_2 e^{r_2} \end{vmatrix}} = \frac{G_0 r_2 e^{r_2}}{r_2 e^{r_2} - r_1 e^{r_1}} \qquad B_1 = \frac{\begin{vmatrix} 1 & G_0 \\ r_1 e^{r_1} & 0 \end{vmatrix}}{\begin{vmatrix} 1 & 1 \\ r_1 e^{r_1} & r_2 e^{r_2} \end{vmatrix}} = \frac{-G_0 r_1 e^{r_1}}{r_2 e^{r_2} - r_1 e^{r_1}}$$

$$\frac{G}{G_0} = \frac{1}{r_2 e^{r_2} - r_1 e^{r_1}} \left\{ r_2 e^{r_2} e^{r_1 x} - r_1 e^{r_1} e^{r_2 x} \right\}$$

at $x = 1$

$$J = qG - \frac{D}{L}\frac{dG}{dx} = qG$$

$$\frac{J}{qG_0} = \frac{G}{G_0 \big|_{x=1}} = \frac{\exp(P_e)(r_2 - r_1)}{r_2 \exp(r_2) - r_1 \exp(r_1)}$$

$$\frac{\text{Case 1 Flux}}{\text{Case 2 Flux}} = \frac{1}{P_e} \frac{\left[r_2 \exp(r_2) - r_1 \exp(r_1) \right]}{\left[\exp(r_2) - \exp(r_1) \right]}$$

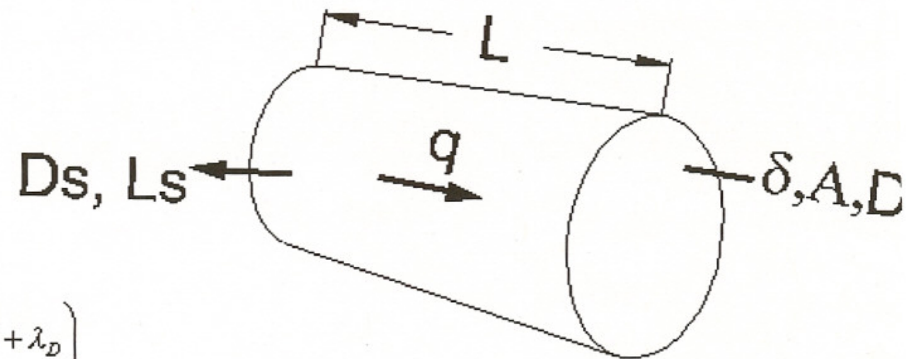
Parameter Values for 1-D Steady State Diffusion Model

PARAMETER VALUES FOR 1-D STEADY STATE DIFFUSION MODEL

1. Elemental Parameters

The parameters of the 1-D Diffusion model are:

$$P_e = \frac{qL}{D}$$



$$B_a = \frac{\lambda L^2}{D}$$

$$where\ \lambda = \left(\frac{\lambda_B}{H} + \lambda_D\right)$$

$$and\ \lambda_D = \frac{D_s}{L_s}\frac{\delta}{A}$$

Therefore, the elemental parameters that need to be specified are:

L = Length of domain [cm]

H = Dimensionless Henry's Law

D = Effective Diffusion Coefficient in Conduit [cm^2 / sec]

λ_B = Microbial Decay Constant [1/ sec]

q = Specific Dicharge for Air Phase

D_s = Effective Diffusion Coefficient of Surrounding Medium [cm^2 / sec]

L_s = Length from Conduit Edge to Zero Concentration [cm]

∂ = Circumference of Conduit [cm]

A = Cross-Sectional Area of Conduit [cm^2]

2. Geometric Parameters

Geometric parameters that need to be specified by user:

L - Length of domain in [cm]

δ - Circumference of conduit [cm]

A - Cross-sectional area of conduit [cm^2]

3. Chemical Parameters

Compounds of interest that need to be specified by user:

Chemical

Temperature of chemical in conduit

H - Dimensionless Henry's Law Coefficient (see Baehr et al. WRR 35(1) p 127-136 Jan. 1999 Table 3 below for compilation of major VOC compounds)

Table 3. Values of H, the Dimensionless Henry's Law Coefficient, for Selected Volatile Organic Compounds as a Function of Temperature

	5°C	10°C	15°C	20°C	25°C	30°C
methyl. tert-butyl ether (MTBE)	0.0043	0.0069	0.0109	0.0169	0.0259	0.0391
naphthalene	NA	NA	NA	NA	0.0174	NA
trichloromethane (chloroform)	0.0542	0.0713	0.0928	0.1197	0.1531	0.1942
1,1-dichloroethane	0.0754	0.1018	0.1361	0.1801	0.2359	0.3063
benzene	0.0932	0.1164	0.1441	0.1771	0.2160	0.2618
o-xylene	0.1018	0.1241	0.1502	0.1806	0.2157	0.2560
ethylbenzene	0.1116	0.1473	0.1924	0.2490	0.3194	0.4062
toluene	0.1289	0.1570	0.1899	0.2281	0.2722	0.3229
m- and p-xylene	0.1489	0.1806	0.2175	0.2602	0.3094	0.3656
cis- 1,2-dichloroethene	NA	NA	NA	NA	0.3069	NA
trichloroethylene (TCE)	0.1944	0.2386	0.2907	0.3516	0.4226	0.5046
chloromethane	NA	NA	NA	0.3900	...	...
tetrachloroethylene (PCE)	0.3286	0.4050	0.4953	0.6014	0.7254	0.8692
1,1,1-trichloroethane (TCA)	0.3579	0.4301	0.5134	0.6090	0.7181	0.8419
carbon disulfide	NA	NA	NA	0.5822	NA	NA

NA, data were not available to compute temperature dependence. Temperature dependence is calculated according to the van't Hoff equation, d ln(H)/dT = AH14- _J RT 2 where H is the dimensionless Henry's law coefficient, T is temperature in kelvins, R is the gas constant R = 8.205783 x 10-5 (meter3 atmospheres)/(moles Kelvin), and AHliny is the change in enthalpy associated with aqueous-gaseous phase partitioning. AHH_ is assumed to be constant with respect to temperature and was calculated from data reported by Robbins [1993] for MTBE, PCE, TCE, TCA, benzene, toluene, xylenes, and ethylbenzene. Data for chloromethane, chloroform, cis-1,2 dichloroethene, 1,1-dichloroethane, and naphthalene from Mackay and Shiu [1981]. Value for carbon disulfide from Howard [1991].

4. Decay Parameters

Parameters provided but allow for user override.

λ_B - Microbial decay constant [1/sec]

$\lambda_B = 0$	No degradation
$10^{-5} < \lambda_B < 10^{-7}$	Referenced range for aerobic BTEX degradatior
$\lambda_B < 10^{-8}$	MTBE degradation

Iconic summary for menu:

$\lambda_B = 0$	None
$\lambda_B < 10^{-9}$	Very low
$10^{-9} < \lambda_B < 10^{-8}$	Low (eg MTBE)
$10^{-7} < \lambda_B < 10^{-6}$	Intermediate (eg BTEX)
$10^{-5} < \lambda_B < 10^{-4}$	High
$\lambda_B > 10^{-4}$	Very high

5. Conduit Diffusion Coefficients

Parameters provided but allow for user override.

D - Effective diffusion coefficient in 1-D conduit [cm^2/sec]

$$D = d\theta_a\tau$$

d = Bulk air diffusion coefficient for compounds of interest and all temperature ranges

$d \sim .08\ cm^2/sec$ is a good approximation (Fuller, et al. 1966)

$$0 < \theta_a < \phi$$

ϕ = porosity

$$\tau = \frac{\theta_a^{7/3}}{\phi^2}$$

τ = Millington and Quirk model

Millington and Quirk overestimates for natural sediments, but for conduit fill (gravel, coarse sand) material should be appropriate (Fischer et al. 1996)

a. Gravel (usually dry)

$\phi = .35$ $\theta_a = .05$

b. Medium Sand (drained)

$\theta_a = \phi$

	$D = 0.02$	maximal
	$D = 0.01$	high
	$D = 0.005$	moderate
	$D = 0.001$	low

Values for D are reported in Lahvis et. al. (1999).

6. Surrounding Medium Diffusion Parameters

Parameters provided but allow for user override.

D_S = Effective diffusion coefficient in medium surrounding 1-D conduit [cm²/sec]

L_s = Length from conduit edge to zero concentration [cm]

Input as lumped parameter.

$$\frac{D_s}{L_s} \qquad \frac{cm^2 / \sec}{cm} = cm / \sec$$

In general $D_s \le D$ because the surrounding medium will be natural material and generally less diffusive than conduit.

$L_s = 10\ cm$	very sharp gradient
$50\ cm$	moderate
$100\ cm$	low

$$\frac{D_s}{L_s} = \frac{.02}{10} = .002$$ maximal diffusive loss to surroundings

$$\frac{D_s}{L_s} = \frac{.01}{50} = .0002$$ average

$$\frac{D_s}{L_s} = \frac{.02}{100} = .0002$$ low

Ask user if surrounding medium is more or less diffusive than conduit in which case $\frac{D_s}{L_s}$ constrained or else user may override default.

7. Specific Discharge for Air Phase

q = specific discharge for air phase [cm/sec]

Basis for estimate Darcy's Law

$$q = -\frac{k}{\mu}\frac{dP}{dx}$$

P = Pressure [g/(cm sec^2)]

k = Air-phase permeability [cm^2]

μ = Dynamic viscosity of fluid [g/(cm-sec)]

1 atm= 1,013,250 $\frac{g}{cm \sec^2}$ = 406.8" water (Joss and Baehr, 1995)

μ ~.000176 g/(cm-sec) (Joss and Baehr, 1995)

Typical values of air-phase permeability from Freeze and Cherry (1979):

k = 10^{-9}	fine sand	
k = 10^{-8}	medium sand	Freeze & Cherry
k = 10^{-7}	coarse sand	
k = 10^{-6}	gravel	

User can specify pressure drop gradient inches H_2O over conduit distance or specific discharg

	q	
1 inch over 10 meters & k=10^{-8} ~	10^{-4} $cm/\sec$	very high
1 inch over 100 meters & k =10^{-8}~	10^{-5} $cm/\sec$	high
~	10^{-6} $cm/\sec$	moderate
~	10^{-7} $cm/\sec$	low
.1 inch over 20 meters & k =10^{-9}~	10^{-8} $cm/\sec$	minimal

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