United States Environmental Protection Agency
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EMSOFT User's Guide

Update to EMSOFT User's Guide
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PREFACE

The National Center for Environmental Assessment (NCEA) has prepared this manual and model to help assessors quantify contaminant air emissions from soils. This manual and model were first published in 1993 to provide technical support to the many EPA program offices, EPA regional offices, State and other organizations requesting assistance on exposure assessment methodologies pertaining to volatilization of compounds from soil.

Air emissions from contaminated soils is a potential exposure route commonly examined when conducting an exposure assessment. In 1986, EPA published the report *Development of Advisory Levels for Polychlorinated Biphenyls (PCBs) Cleanup* which described a model estimating PCB emission rates from contaminated soils under four different scenarios (i.e., steady state with and without a soil cover and unsteady state with and without a soil cover). This project is a continuation of work conducted under EPA Contract No. 68-DO-0100 performed by ENSR Consulting and Engineering who served as the primary contractor. That effort resulted in the August 1993 draft report entitled *"EMSOFT: Exposure Model for Soil-Organic Fate and Transport."* This report documents a screening model that primarily ranks the relative volatilization potential of different organic chemicals. The EMSOFT Model is largely based on the work and theories developed by William A. Jury.

An internal EPA peer review resulted in several favorable comments to the August 1993 EMSOFT draft. Modification to certain model codes and a few model enhancements were recommended. This resulted in an update of the original EMSOFT model (Version 1.0) under EPA Contract No. 68-D3-0035 performed by Environmental Quality Management, Inc. (EQ) under subcontract to E.H. Pechan and Associates, Inc. (Pechan) in August 1996. Since that time, additional comments have been received, the majority of which requested a Microsoft® Windows version of the model. This effort addresses these comments with the production of a version of the EMSOFT model designed to operate in a Windows environment (Version 2.01). This work was completed by EQ under EPA Purchase Order Number 2W-0316-NALX. Ms. Amina Wilkins of NCEA was the EPA Project Manager

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The National Center for Environmental Assessment (NCEA) was responsible for the preparation of this model and manual.

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CONTENTS

CONTENTS (continued)

FIGURES

TABLES

What's New...

This version of the EMSOFT model (Version 2.01) converts the previous DOS model into a Windows environment. All the user interface screens have been updated to run under a Windows operating system. While all the screens remain the same for the most part, there are some subtle differences.

1. The method for saving data files is slightly different by using a button to activate a Windows-based save dialog. This also holds true for retrieving old data files.

2. Chemical data files will now use a .ECF file extension. This is a result of predefined Windows file extension which reserves use of the .CHM for other functions within the Windows registry. While the old DOS-based (.CHM) chemical files can be used within the new version, it is suggested that they be renamed to the .ECF extension to avoid conflicts.

3. Users should not type in the file extensions when saving files as the program will assign the appropriate extension for later retrieval.

4. To navigate through the data input fields, the <TAB> key or the mouse must be used.

5. To switch to another application once the model is executed, the user must use <ALT> + <TAB>, as the model will not minimize during the middle of a run. However, EMSOFT can be minimized before or after a run is executed.

6. Unlike the previous DOS version, all data files saved during a model run are available upon restarting without having to first exit (and re-start) the model.

7. Help screens can be accessed during execution of the model to explain the meaning of model input parameters.

SECTION 1

INTRODUCTION

This manual provides documentation for using EMSOFT (Exposure Model for Soil-Organic Fate and Transport). The model code was developed by ENSR Consulting and Engineering of Acton, Massachusetts, under Work Assignment 92-04 of the U.S. Environmental Protection Agency (EPA) contract number 68-DO-0100 and revised by Environmental Quality Management, Inc. (EQ) of Durham, North Carolina, under Work Assignment II-78 of EPA contract number 68-D3-0035, and under Work Assignment 2-35 of EPA contract number 68-D98-052.

Volatilization of organic chemicals from contaminated soils to the atmosphere and subsequent inhalation represents a potentially significant human exposure pathway. This manual describes a screening model that may be used to assess the potential for such exposure to occur and quantify the mass flux of contaminants to the atmosphere over time. Mass fluxes can then be input to an atmospheric dispersion model to calculate exposure concentrations. Ingestion of contaminated soil and dermal contact are also potentially important exposure pathways. This model can also be used to calculate chemical concentrations in surficial soil layers over time for assessment of these exposures. The model addresses situations in which contaminated soils are located at the surface and buried beneath a clean soil cover.

EMSOFT is based largely on the work of Jury et al. (1983, 1990). The nucleus of the model is formed from the code SCREENB (Jury, undated). This code was modified substantially to provide a convenient Microsoft® Windows user interface and enhanced calculation capabilities for the EMSOFT model. As Jury et al. emphasize in their papers, the model as formulated is properly called a screening model. This means that it is useful primarily in ranking the relative volatilization potential of different organic chemicals, and not necessarily in predicting actual chemical fluxes and concentrations under field conditions. The user is advised to consider the potential variation of input parameters and to explore and quantify the impacts of assumptions on the uncertainty of model results.

A user-friendly Windows interface has been designed to facilitate the entering of input data and the viewing of model results. The user moves through a set of input screens, providing the necessary data either manually or from previously developed input files, and selecting the desired calculation options. With the complete set of input parameters specified, EMSOFT performs the requested calculations. Results can then be viewed in a series of output screens. An option is provided for returning to the front end of the software to solve a new problem.

This manual is organized into six sections:

- Introduction - background on the model is provided
- Theory - the model equations and their development are explained
- Model Application - step-by-step instructions are provided for implementing the model
- Verification - the model is verified by comparing its results to published results
- Validation - the model's performance is evaluated by simulating the conditions reported for several flux measurement studies and comparing results
- References - literature resources used in developing the model are listed.

SECTION 2

THEORY

Organic chemical fate and transport within soils is determined by a number of physical and chemical processes. This section presents the theoretical framework on which EMSOFT is based, taking into account the most significant of these processes. The model is derived from the differential equation and boundary conditions that describe vertical transport of a chemical in a uniform soil. The fundamental theoretical development of this model was performed by Jury et al. (1983, 1990). Notation identical to that of Jury et al. is used here so that those who wish to consult the original papers can do so without difficulty.

2.1 MODEL SETTING

Consider an idealized soil column with uniform properties throughout (porosity, water content, bulk density, fractional organic carbon content, and vertical water flux), extending from the surface to an infinite depth. Initially, a uniform concentration of a chemical is present within the soil matrix (in the aqueous, gaseous, and solid phases) from the surface down to some finite depth. Over subsequent time, the chemical advects (as pore water moves upward or downward), degrades, diffuses, and volatilizes from the surface. At the surface, there is a stagnant air boundary layer across which diffusion occurs. The chemical concentration at the top of the boundary layer is assumed to be zero (i.e., there is sufficient wind velocity to carry away vapor-phase chemical above the boundary layer). Other assumptions are that a linear equilibrium liquid-solid partition relationship is valid (this will generally remain true for low aqueous concentrations) and a linear equilibrium liquid-vapor partition relationship is valid (this should be true up to vapor saturation levels). These simplifications are necessary in order for an analytical expression to be derived for concentration as a function of depth and time and surface flux as a function of time.

2.2 GOVERNING EQUATIONS

For the above conditions, the mass conservation equation for a chemical subject to first-order decay is:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_S}{\partial z} + \mu C_T = 0 \tag{1}$$

where C_T = Mass of solute per unit of soil volume (g/m^3)

J_s = Solute mass flux per unit of soil area per unit time ($g/m^2/day$)

μ = Net degradation rate (per day)

t = Time (day)

z = Soil depth (m).

The solute mass flux, J_s, can be written as:

$$J_S = -D_G \frac{\partial C_G}{\partial z} - D_L \frac{\partial C_L}{\partial z} + J_w C_L \tag{2}$$

where D_G = Soil-gas diffusion coefficient (cm^2/day)

D_L = Soil-liquid diffusion coefficient (cm^2/day)

C_G = Concentration in the gas phase ($\mu g/cm^3$)

C_L = Concentration in the liquid phase ($\mu g/cm^3$)

J_w = Water flux (cm/day).

D_G is related to the air gas diffusion coefficient according to the Millington-Quirk model:

$$D_G = \frac{a^{10/3}}{\varphi^2} D_G^{air} \tag{3}$$

where a = Soil air content (dimensionless)

φ = Soil porosity (dimensionless)

D_G^{air} = Air-gas diffusion coefficient (m^2/day).

The soil-water diffusion coefficient is calculated using an analogous equation:

$$D_L = \frac{\theta^{10/3}}{\varphi^2} D_L^{water} \tag{4}$$

where θ = Soil volumetric water content (dimensionless)

D_L^{water} = Water-liquid diffusion coefficient (m^2/day).

The total concentration, C_T, is a combination of concentrations in the solid, liquid, and gas phases:

$$C_T = \rho_b C_S + \theta C_L + a C_G \tag{5}$$

where ρ_b is the soil bulk density. It can also be expressed in terms of the concentration in any one of the individual phases by using the air-water and water-soil equilibrium partitioning relationships:

$$C_T = R_S C_S = R_L C_L = R_G C_G \tag{6}$$

where

$$R_S = \rho_b + \frac{\theta}{K_D} + \frac{aK_H}{K_D} \tag{7}$$

$$R_L = \rho_b K_D + \theta + aK_H \tag{8}$$

$$R_G = \frac{\rho_b K_D}{K_H} + \frac{\theta}{K_H} + a \tag{9}$$

represent the partition coefficients for the solid, liquid, and gas phases, respectively, which give the ratio of the total concentration to the concentration in each phase. In these equations, K_D is the soil-water partition coefficient and K_H is the Henry's law constant, which describes equilibrium partitioning between air and water.

Equations 6 through 9 can be used to express the mass flux, J_s (Equation 2), in terms of total concentration:

$$J_S = -D_E \frac{\partial C_T}{\partial z} + V_E C_T \tag{10}$$

where D_E is the effective diffusion coefficient:

$$D_E = \frac{D_G}{R_G} + \frac{D_L}{R_L} = \frac{K_H D_G D_L}{R_L} \tag{11}$$

and V_E is the effective solute velocity:

$$V_E = \frac{J_w}{R_L} \tag{12}$$

Equation 10 can be substituted into Equation 1, yielding an expression in terms of total concentration:

$$\frac{\partial C_T}{\partial t} = D_E \frac{\partial^2 C_T}{\partial z^2} - V_E \frac{\partial C_T}{\partial z} - \mu C_T \tag{13}$$

Equation 13 can now be solved using appropriate initial and boundary conditions.

The initial condition is simply that down to some depth L, the total concentration is equal to a constant value, C_o. Below this depth, the initial concentration is zero. The upper boundary condition is represented by a stagnant boundary layer condition. Mathematically, this can be stated as:

$$J_S(0,t) = -hC_G(0,t) \tag{14}$$

where h is the transport coefficient across the stagnant boundary layer of thickness d, and $C_G(0,t)$ is the gas concentration at the soil surface. The gas concentration at the top of the boundary layer is assumed to be zero. Equation 14 can be rewritten in terms of total concentration using Equations 10 and 6:

$$-D_E \frac{\partial C_T}{\partial z} + V_E C_T = -H_E C_T \tag{15}$$

where $H_E = h/R_G$. The lower boundary condition is that the total concentration is zero at $z = \infty$.

2.3 SOLUTION OF EQUATIONS

Equation 13 can be solved analytically with the above initial and boundary conditions using the Laplace transform method. The resulting solution is:

$$C_T(z,t,L) = +\frac{1}{2} C_0 \exp(-\mu t)\left[erfc\left(\frac{z - L - V_E t}{2\sqrt{D_E t}} \right) - erfc\left(\frac{z - V_E t}{2\sqrt{D_E t}} \right) \right]$$

$$+\frac{1}{2}C_0\exp(-\mu t)\left(1+\frac{V_E}{H_E}\right)\exp\left(\frac{V_E z}{D_E}\right)\left[erfc\left(\frac{z+L+V_E t}{2\sqrt{D_E t}}\right)-erfc\left(\frac{z+V_E t}{2\sqrt{D_E t}}\right)\right] \quad (16)$$

$$+\frac{1}{2}C_0\exp(-\mu t)\left(2+\frac{V_E}{H_E}\right)\exp\left(\frac{H_E(H_E+V_E)t+(H_E+V_E)z}{D_E}\right)$$

$$\times\left[erfc\left(\frac{z+(2H_E+V_E)t}{2\sqrt{D_E t}}\right)-\exp\left(H_E\frac{L}{D_E}\right)erfc\left(\frac{z+L+(2H_E+V_E)t}{2\sqrt{D_E t}}\right)\right]$$

where erfc is the complementary error function.

The volatilization flux at the surface can be evaluated using Equations 10, 15, and 16:

$$J_S(t,L)=+\frac{1}{2}C_0\exp(-\mu t)V_E\left[erfc\left(\frac{V_E t}{2\sqrt{D_E t}}\right)-erfc\left(\frac{L+V_E t}{2\sqrt{D_E t}}\right)\right]$$

$$+\frac{1}{2}C_0\exp(-\mu t)(2H_E+V_E)\exp\left(\frac{H_E(H_E+V_E)t}{D_E}\right) \quad (17)$$

$$\times\left[\exp\left(\frac{H_E L}{D_E}\right)erfc\left(\frac{L+(2H_E+V_E)t}{2\sqrt{D_E t}}\right)-erfc\left(\frac{(2H_E+V_E)t}{2\sqrt{D_E t}}\right)\right]$$

With these solutions for a single layer of contamination at the surface, we can build solutions for arbitrary numbers of contaminated layers by applying the principle of superposition. For example, the total concentration as a function of depth and time for a layer of thickness D buried at a depth of DB below the surface would be calculated as $C_T(z,t,D+DB)-C_T(z,t,DB)$. For n layers, each with a thickness D_i and buried at a depth of DB_i below the surface, the total concentration as a function of depth and time would be:

$$C_{BT}(z,t) = \sum_{i-1}^{n} \left[C_T\left(z,t,D_i + DB_i\right) - C_T\left(z,t,DB_i\right) \right] \qquad (18)$$

Using this equation, one could discretize a soil contamination profile into layers of constant concentration and calculate resulting concentrations and fluxes.

In addition to calculating values at a particular time, time-averaged properties are also of interest, such as in assessing inhalation, soil ingestion, and dermal contact exposures over some specific period. Time-averaged concentrations and fluxes are obtained by integrating the variable of interest over time and dividing by the time period. Similarly, concentrations can be averaged over depth by integrating with respect to z and dividing by the depth of interest.

The EMSOFT model includes the analytical solution of Jury et al. (1990) to the integral for time-averaged flux thereby eliminating the possibility of mass balance violations (e.g., the cumulative loss by volatilization over time cannot exceed the total initial mass in the soil).

2.4 DISCUSSION OF MODEL ASSUMPTIONS

Several simplifying assumptions have been made to develop the model upon which EMSOFT is based (Jury et al., 1983). These assumptions are necessary to derive an analytical solution (i.e., a single equation expressing concentration or flux as a function of depth and time). Important assumptions and their effect on model output are discussed below.

- Steady porewater flux. The vertical movement of porewater is assumed to occur at a constant rate over the duration of a model simulation. Under natural conditions, the porewater flux is rarely if ever constant, but instead varies with changes in rainfall and evaporation. (To account for this variability, however, would require a more complex numerical model.) A downward porewater flux will result in a lower volatilization rate than an upward porewater flux. Specification of this parameter will depend on the data available for the site and how conservative the user wants to be for the situation under consideration. Except for rare instances, a net downward porewater flux is typically assumed over long periods of time.

- Homogeneous soil properties. Although the model assumes that soil properties are homogeneous, naturally occurring soils are usually heterogeneous, with properties that change with depth. These properties include fraction organic carbon, water content, porosity, and bulk density. The model user will need to carefully consider the characterization of soil properties before assigning model input parameters.

Results will be sensitive to the fraction organic carbon, because this determines how strongly a compound will be retained by the soil. A high fraction organic carbon will result in less chemical volatilization than a low fraction organic carbon. Water content can also have a significant effect on the volatilization rate, as demonstrated by Jury et al. (1984a). In general, a lower water content results in a higher volatilization rate. Model results will be less sensitive to the porosity and bulk density. These parameters are also easier to estimate than the fraction organic carbon and water content.

- Chemicals present in dissolved form at low concentrations. The equilibrium partitioning relationships used in the model are no longer valid when a pure phase of a chemical or a concentrated mixture of chemicals are present. Thus, the model should not be applied in situations where a concentrated/pure chemical phase exists. Please note that attempts to apply EMSOFT results to chemical mixtures one chemical at a time and then combining the results, will produce misleading/erroneous concentrations because the EMSOFT model uses Henry's law and not Rault's law. Partial pressures for each individual chemical varies as a function of concentration, temperature, and the number of chemicals present in vapor phase.

  Calculation of the soil concentration above which a pure phase is present for individual components of a mixture typically requires complex thermodynamic mass balance solutions. For a single compound in soil, however, this concentration (C_{sat}) may be estimated from U.S. EPA (1996):

$$C_{sat} = \frac{S}{\rho_b}\left(K_D \rho_b + \theta + K_H a\right) \tag{19}$$

where C_{sat} = Soil saturation concentration, mg/kg

S = Solubility in water, mg/l

K_D = Soil-water partition coefficient l/kg

ρ_b = Soil bulk density, kg/l

θ = Soil volumetric water content, l/l

K_H = Henry's law constant, dimensionless

a = Soil volumetric air content, l/l.

The calculated value of C_{sat} may be used as a preliminary estimate of the soil concentration below which the EMSOFT model is applicable. The user is referred to U.S. EPA (1992) for more information on determining the likelihood of free-phase contaminants in soil when multiple contaminants are present at a site.

- Volatilization at the surface occurs through a stagnant air boundary layer of thickness d. This assumption is physically realistic, but brings with it the difficulty in specifying the boundary layer thickness, which cannot be directly measured. Guidance is therefore provided in this manual on how to calculate it, and typical values are also given. Everything else being equal, a smaller boundary layer thickness will result in increased volatilization. This is particularly true for those chemicals whose diffusion rate through the air layer is less than the flow to the surface by diffusion or mass flow. This behavior is determined primarily by a chemical's Henry's Law constant. For chemicals with K_H greater than 2.65×10^{-5}, volatilization is not strongly dependent on d. Chemicals with K_H less than 2.65×10^{-5}, however, exhibit a volatilization rate that is strongly dependent on d.

SECTION 3

MODEL APPLICATION

This section provides step-by-step instructions on how to implement EMSOFT. The model has a user-friendly interface consisting of a sequence of 12 individual graphical screens. The user provides data, selects input and output options, and views model results via these screens. Files are also written, if desired, to preserve input data and output for future use and analysis. Help screens can be accessed during execution of the model to explain the meaning of model input parameters.

3.1 INSTALLING AND RUNNING THE MODEL

The model is supplied in a self extracting zipped file (Emsoftzip.exe). To install the model on the hard drive of your computer, copy Emsoftzip.exe into the directory or subdirectory in which you want the program to reside. It is recommended that the user create a directory named "Emsoft." Once the Emsoftzip.exe file has been copied into this directory, from Windows explorer, double click on this file to execute the unzipping sequence. This will extract three (3) files into this directory. The files that will be extracted are:

- Emsoft.exe
- Example.dat
- Example.ecf.

Only one file, Emsoft.exe, is required to run the EMSOFT model. The other two files, Example.dat and Example.ecf, are example data files which can be loaded into the EMSOFT model. It is recommended that a subdirectory be created called "Data" within the Emsoft directory and these two files be copied and/or saved here for ease in data management. Any files created from a previous EMSOFT version should also be moved into this subdirectory.

To execute the model you must double-click the Emsoft.exe file. A desktop icon can be created for convenience to the user. If this is desired, please refer to the Microsoft® Windows User's guide under creating a shortcut. The computer on which the model is run must have an 8087 math coprocessor.

3.2 BASICS: MOVING AROUND THE SCREENS AND MAKING SELECTIONS

The user enters data into and selects options from predefined regions (input fields) on the interface screens. The cursor indicates the currently active input field. The user can move the cursor within a screen using the keyboard or a mouse. With the keyboard, cursor movement is controlled by the <TAB> key. The <TAB> key moves the cursor to the next input field in a screen.

Most of the screens have a NEXT button, and an EXIT button. A button can be "pressed" by positioning the pointer on it and clicking the mouse or tabbing to the button and pressing <ENTER>. Pressing the NEXT button validates the choices and input parameters entered on the screen. It also causes control to be transferred to the next model screen; therefore, the user should be satisfied with the selections made before proceeding. Pressing the EXIT button allows the user to terminate execution of the model, and return to the user's Windows desktop. To prevent accidental model termination, the user is requested to confirm that model termination is in fact desired. The user may also advance to the next screen by pressing <ENTER> while in the input fields.

The input screens also have a BACK button. This allows the user to return to a previous input screen if a previously entered input parameter needs to be changed before running the model. Note that if you enter input parameters on a screen and want to return to the previous one, those input parameters will not automatically be saved. If you want to save the input parameters on a screen and return to the previous screen, you must first select NEXT, go to the next screen, and then back up two screens.

3.3 HELP SCREENS

On-line help screens are available to describe many selection options and input parameters. A help screen is displayed by positioning the cursor on the item for which help is needed and

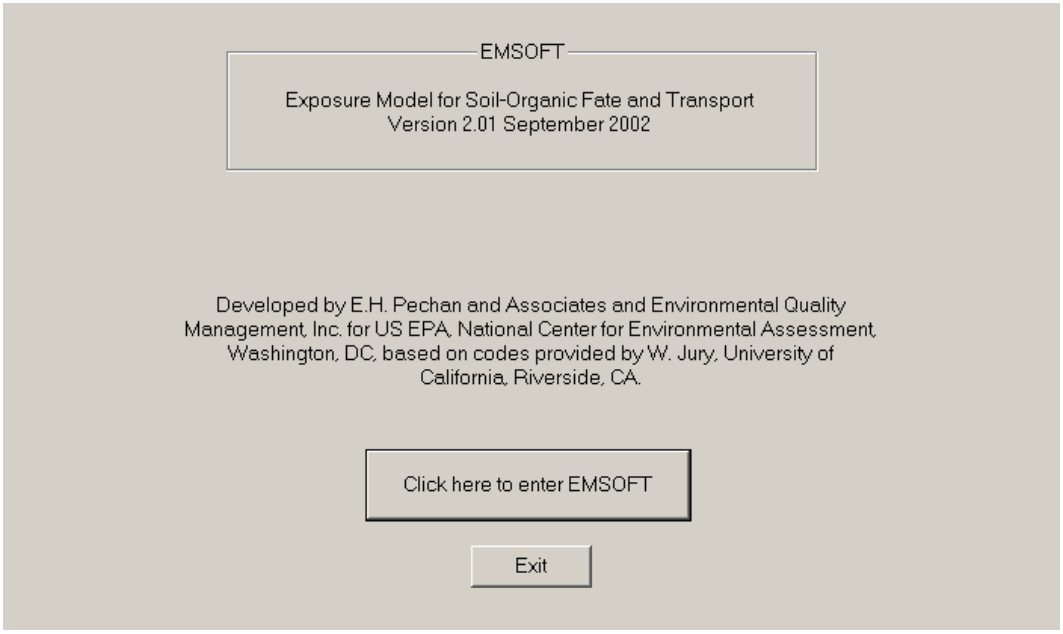
pressing the HELP button. A help screen will be displayed for the item chosen and a short description and instructions will be provided. To leave the help screen and return to the current model screen, press the OK button.

3.4 SCREEN DESCRIPTIONS

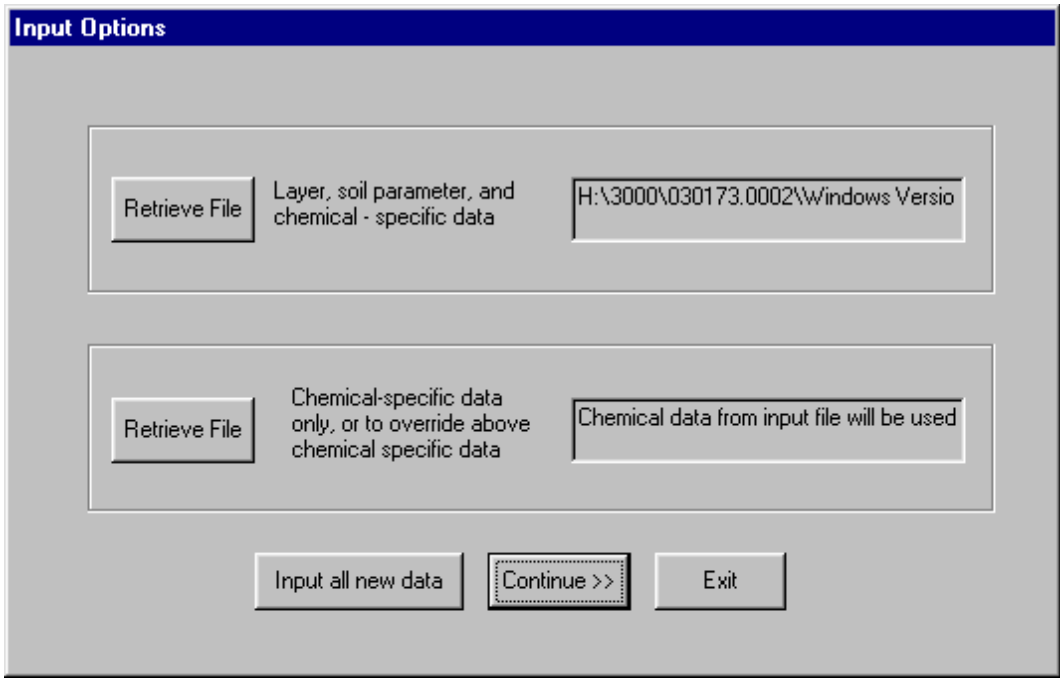
The 12 model interface screens are as follows:

- Screen 1: Title
- Screen 2: Input options
- Screen 3: Output control and calculation options
- Screen 4: Chemical data
- Screen 5: Soil properties and physical constants
- Screen 6: Layer properties
- Screen 7: Input/output save
- Screen 8: Calculation screen
- Screen 9: Flux results
- Screen 10: Soil concentration results
- Screen 11: Print Results
- Screen 12: Restart/Quit.

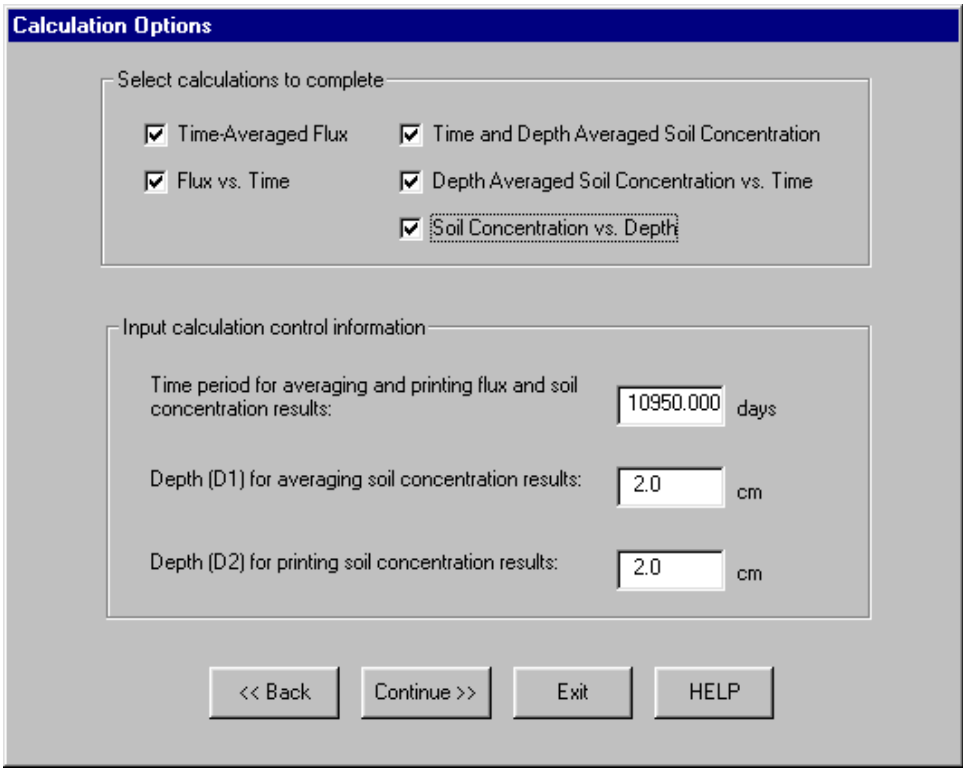
A graphic of each screen is provided on the following pages.



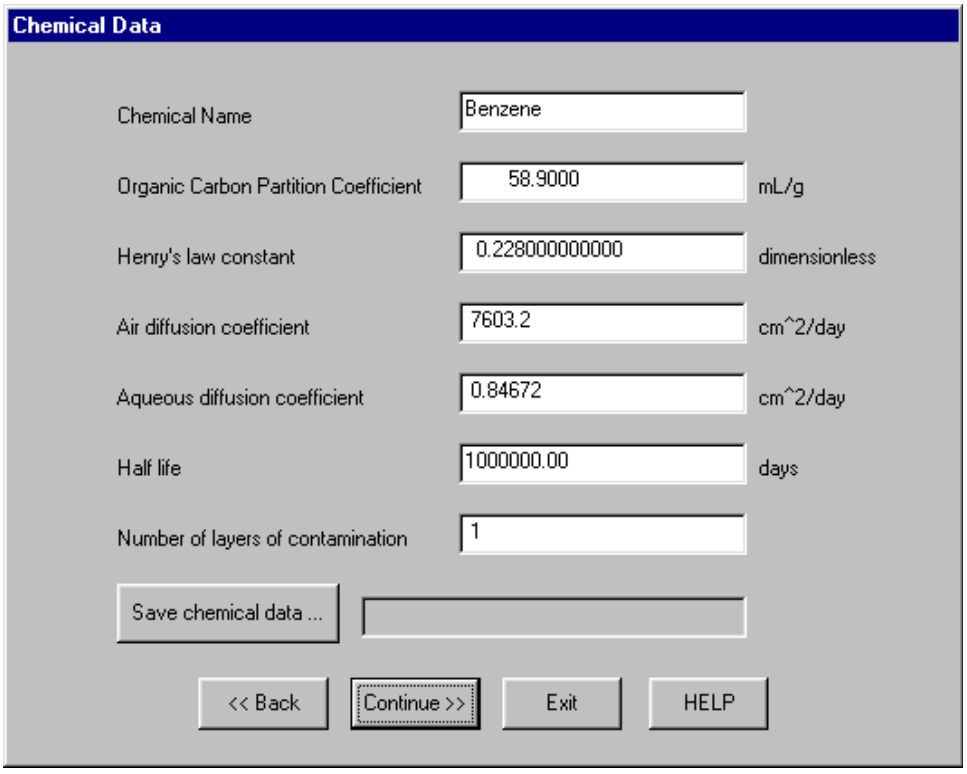
SCREEN 1: Title



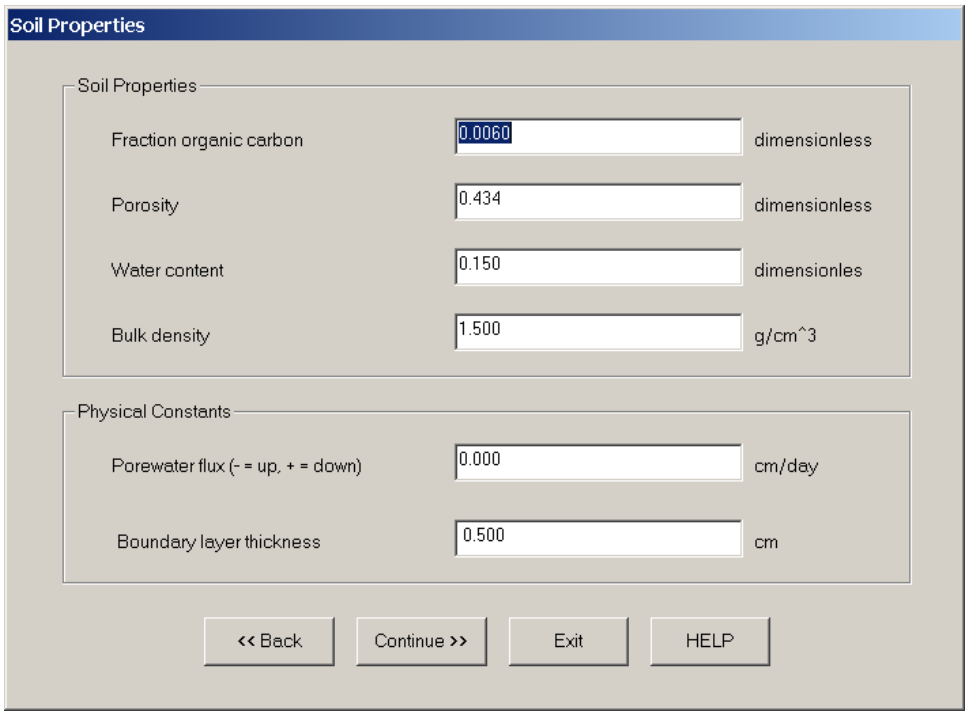
SCREEN 2: Input Options



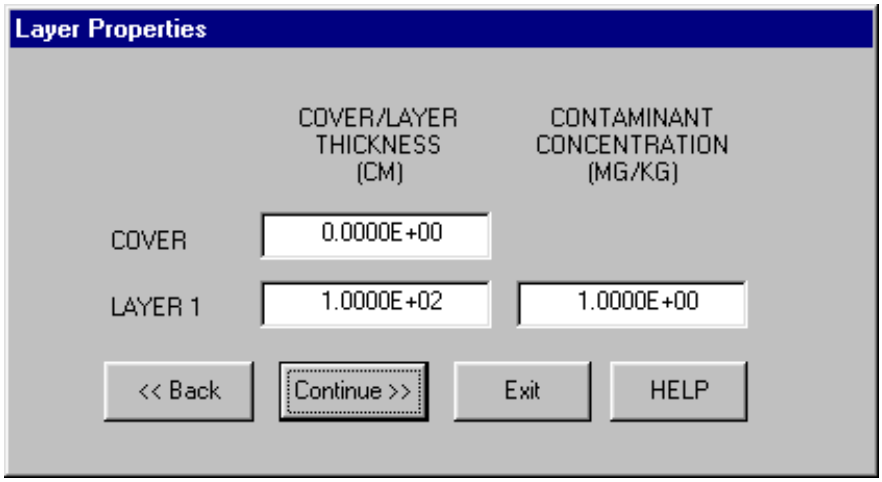
SCREEN 3: Output Control and Calculation Options



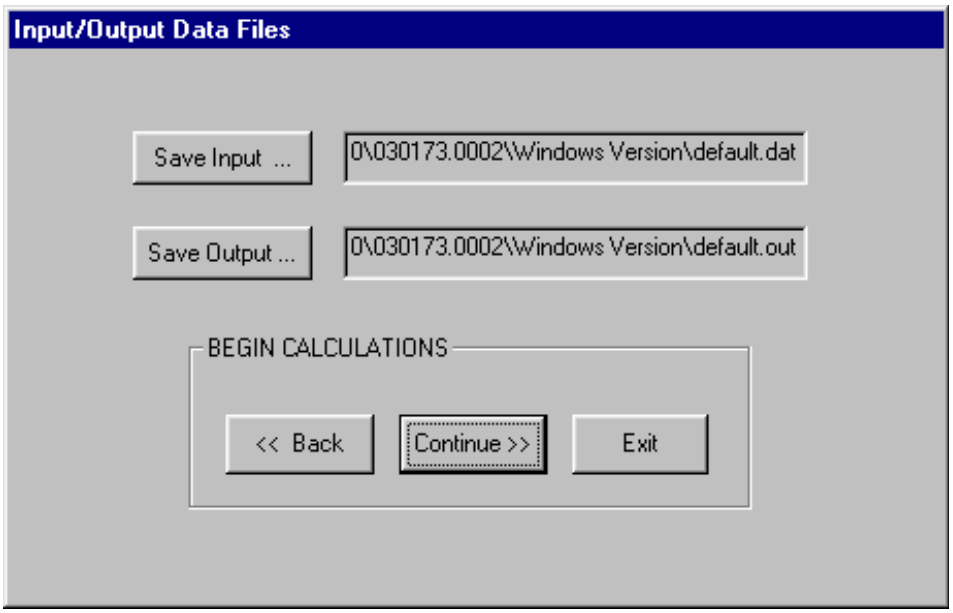
SCREEN 4: Chemical Data



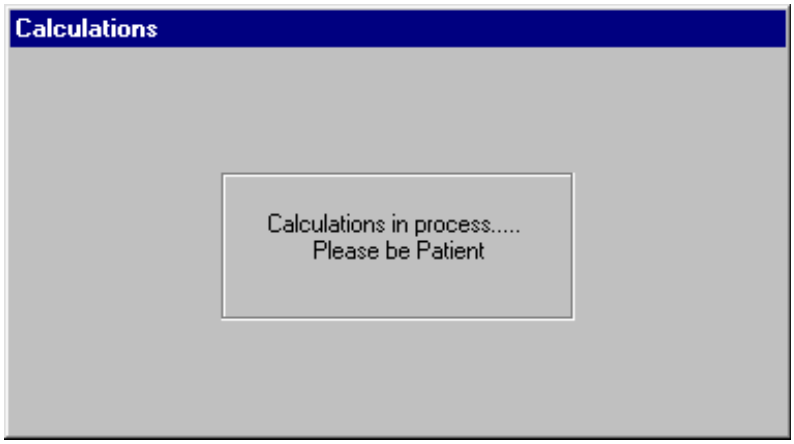
SCREEN 5: Soil Properties and Physical Constants



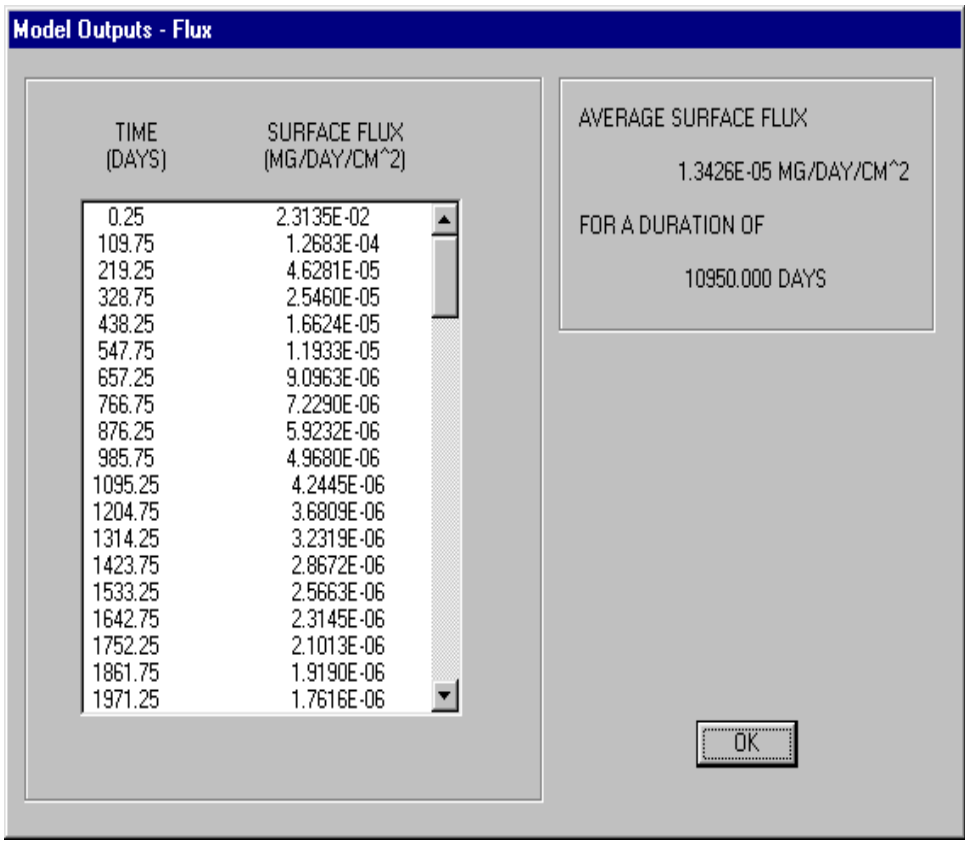
SCREEN 6: Layer Properties



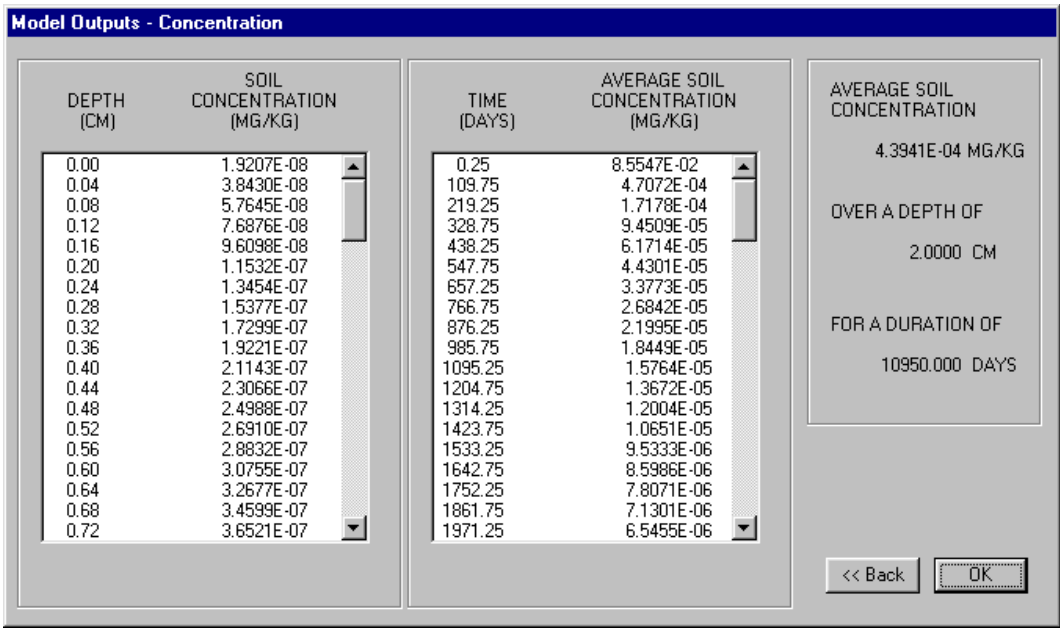
SCREEN 7: Input/Output Save



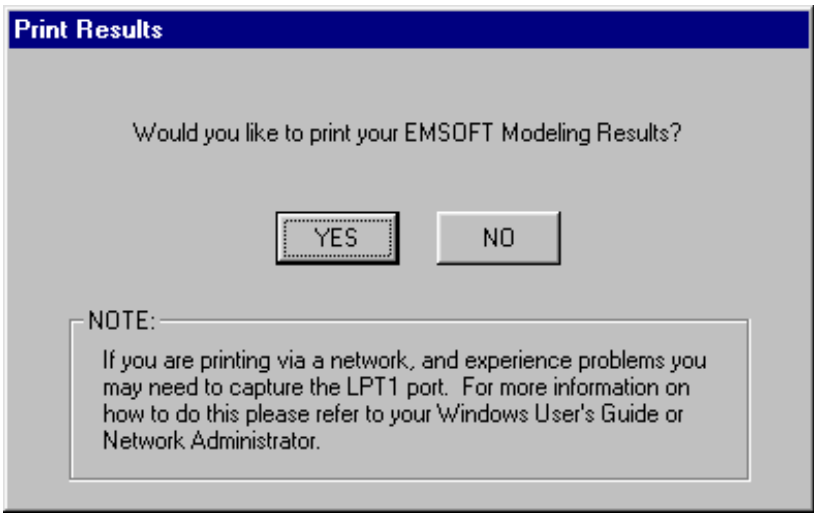
SCREEN 8: Calculation Screen



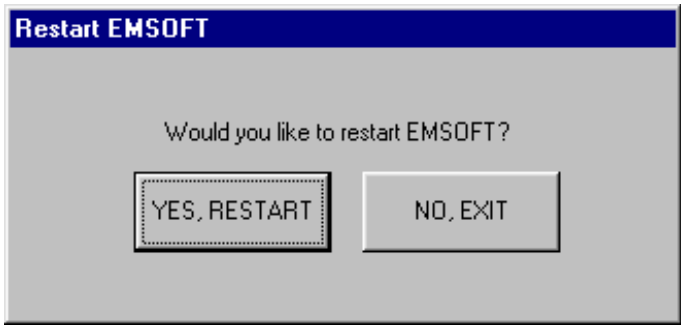
SCREEN 9: Flux Results



SCREEN 10: Soil Concentration Results



SCREEN 11: Print Results



SCREEN 12: Restart/Quit

Each screen is described sequentially below as if one were running the model, and instructions for individual input items are given.

3.4.1 Screen 1: Title

This screen displays the title of the model and acknowledgments. The user continues to the next screen by pressing the "Click here to enter EMSOFT" button. The user may also exit the program by pressing the EXIT button.

3.4.2 Screen 2: Input Options

Several options are available for providing input parameters to the model. This screen allows the user to specify previously created files as the source of some of the input parameters or create new input values. The first option - use of an existing file for all of the soil parameters, chemical properties, and layer information - is selected by pressing the Retrieve File button to the left of the text. A select file dialog box will appear which lists all previously saved input data files (those having a .DAT file extension). The user may select the desired file with the mouse and click the OPEN button. This will load the selected data file and the file location will be displayed in the appropriate field of the Input Options screen. The user will also notice that the field for chemical data will have changed to read "Chemical data from input file will be used."

The second option - use of an existing file for chemical property data only (which overrides any chemical properties given by the first file if it was selected) - is selected in the same manner as the first option. Available chemical data files (those having the .ECF file extension) are shown in the select file dialog box for the user. Previous EMSOFT users should note the DOS version saved these files with a .CHM extension. Since '.CMH' is a preassigned Windows extension, another extension has been assigned for EMSOFT chemical files saved in the new version. The new version, however, has also been programmed to read the old DOS files with a .CHM extension. Older files should be renamed using Windows Explorer or some other file management tool to ensure that there are no conflicts. Please consult your Windows user's guide for more information.

These options offer several useful features. Using the first option, a given scenario can be rapidly run multiple times without having to re-specify all input parameters. The user might, for example, wish to look at the effects of changing the fraction of organic carbon (foc) variable with all other parameters remaining the same. Or, the same soil properties might be used multiple times

for different chemicals. Using the second option, a library of chemical property files can be built for later retrieval. This will save significant time in performing model runs and sensitivity analyses. For new chemicals that are not listed on Screen 2, the user should proceed to and fill-out Screen 3, and then proceed to Screen 4 where the new chemical data may be input.

3.4.3 Screen 3: Output Control and Calculation Options

The model offers five calculation options:

- Time-averaged vapor flux
- Vapor flux as a function of time
- Soil concentration averaged over a given time and soil depth
- Soil concentration averaged over a given soil depth as a function of time
- Soil concentration as a function of depth at a specific time.

The time-averaged vapor flux is useful for determining average fluxes (and, ultimately, exposure concentrations) during a specified simulation period. The vapor flux as a function of time can also be calculated to determine the time during which the greatest flux, and hence greatest exposure, occurs.

The other three calculation options relate to chemical concentrations within the soil, which may be important in assessing risks associated with soil ingestion, inhalation of particulates, and dermal contact with contaminated soils. First, the chemical concentration within a soil layer measured from the surface can be averaged over the specified simulation period. Second, the average chemical concentration within a soil layer measured from the surface can be calculated at regular time intervals for the duration of the simulation period. Third, the chemical concentration within a soil layer can be calculated to a specified depth at the end of the simulation period.

By mass balance, a mass flux to an underlying water table may also be obtained. It should be remembered, however, that the model assumptions include an isotropic soil column extending to an infinite depth (i.e., no soil column bottom boundary). Shan and Stephens (1995) developed an analytical solution which incorporates a bottom boundary. Comparative results with Jury et al. (1990) indicated that neglecting the water table boundary conditions in dry soils where gas diffusion is significant may lead to underestimation of the mass flux to the aquifer, especially for extended time periods.

One or more calculation options may be selected for any given model run. Some options, however, increase model run time significantly, and therefore only the options of interest should be selected for a given run. An option is selected by positioning the pointer on the option box and clicking the mouse or tabbing to the desired option and pressing the space bar. An option can be de-selected by pressing the space bar or clicking the mouse again.

In order to implement these calculation options, the user must specify the time period and depths of interest. These are entered in the appropriate input fields below the option selection buttons. The time period is specified in units of days with a range of 0.1 to 100,000 days. This time is used as the averaging period for time-averaged quantities (vapor flux and depth-averaged soil concentration) and also the period during which quantities are calculated at regular time intervals (vapor flux and depth-averaged soil concentrations). The soil concentration profile is reported for the end of this time period. Two depths are requested in this screen. The first depth (D1) is used for depth averaging soil concentrations. The second (D2) is the depth down to which the soil concentration profile is calculated. A value between 0.1 and 100 cm must be entered for both D1 and D2 regardless of the EMSOFT calculations to be performed.

3.4.4 Screen 4: Chemical Data

The chemical name, chemical property data, and the number of contaminated layers (maximum of 10) used to discretize the contaminant concentration profile are entered in this screen. The chemical data can also be saved in a file for use in future model runs. Chemical property values can be found in numerous references or obtained from commercially available chemical property databases. Each of the chemical property parameters is briefly described below.

Organic Carbon Partition Coefficient--

This parameter, usually abbreviated as K_{oc}, is a measure of the degree to which the chemical in a dilute solution partitions between water and organic carbon under equilibrium conditions. It is equal to the mass of solute on organic carbon per unit mass of organic carbon divided by the concentration of the solute in solution at equilibrium. Higher values of K_{oc}, therefore, correspond to a greater tendency of a chemical to sorb to organic particles in the soil. K_{oc} is generally expressed in units of ml/g. The soil-water partition coefficient, K_D, is equal to the product of K_{oc} and f_{oc}, the fraction of the soil composed of organic carbon (f_{oc} is discussed later in Section 3.4.5).

Various equations have been developed to estimate K_{oc} for both ionizing and nonionizing organic compounds from aqueous solubilities and K_{ow} values (octanol-water partition coefficients), which have been measured for many chemicals. For example, Hassett et al. (1983) derived the following linear relationships between log(K_{oc}) and log(S), and between log(K_{oc}) and log(K_{ow}):

$$\log K_{oc} = 3.95 - 0.62 \log S \tag{20}$$

$$\log K_{oc} = 0.088 + 0.909 \log K_{ow} \tag{21}$$

where S is the solubility in units of mg/l, and K_{oc} and K_{ow} are in units of ml/g. The reader is referred to U.S. EPA (1996) for a comprehensive discussion of K_{oc} for both organic and inorganic compounds.

Henry's Law Constant--

The Henry's law constant, K_H, is a measure of the degree to which a chemical in solution partitions between water and air under equilibrium conditions. It is equal to the saturated vapor pressure divided by the solubility. This yields units of atm-m^3/gmol. The dimensionless form used in EMSOFT is obtained according to the following equation:

$$K_H = \frac{K'_H}{RT} \tag{22}$$

where K_H' is the Henry's law constant expressed in atm-m^3/gmol, R is the universal gas constant (8.21 x 10^{-5} atm-m^3/gmol-^{o}K), and T is the temperature at standard conditions in ^{o}K. In this EMSOFT version, the value of the chemical-specific Henry's law constant used in the model is user-defined. Literature values of the Henry's Law constant for a specific chemical are typically given at 25^{o}C. Long-term average soil temperatures, however, are normally below this value. The effect of temperature on the Henry's law constant can be dramatic, especially for semi-volatile compounds. For example, reducing the temperature from 25^{o}C to 10^{o}C (a typical subsurface temperature) reduces the value of the Henry's law constant for a volatile compound like benzene by a factor of

approximately one half, while the reduction for a semi-volatile like hexachlorobenzene is approximately one order-of-magnitude. The effect of the value of the Henry's law constant on the final emission flux at the soil surface is linear. At present, the EMSOFT model user must make this correction separately and enter the appropriate value of the Henry's law constant into the EMSOFT model.

The dimensionless Henry's law constant may be corrected for the average soil temperature using the Clausius-Clapeyron relationship [1]:

$$K_H = \frac{\exp\left[- \frac{\Delta H_{v,TS}}{R_C}\left(\frac{1}{T_S} - \frac{1}{T_R} \right) \right] H_R}{RT_S} \qquad (23)$$

where:

K_H	=	Henry's law constant at the average soil temperature, dimensionless
$\Delta H_{v,TS}$	=	Enthalpy of vaporization at the average soil temperature, cal/mol
T_S	=	Average soil temperature, ^oK
T_R	=	Henry's law constant reference temperature, ^oK
H_R	=	Henry's law constant at the reference temperature, atm-m^3/mol
R_C	=	Gas constant (= 1.9872 cal/mol-^oK)
R	=	Gas constant (= 8.205 x 10^{-5} atm-m^3/mol-^oK).

The enthalpy of vaporization of the compound at the average soil temperature ($\Delta H_{v,TS}$) can be approximated from the enthalpy of vaporization at the normal boiling point by [2]:

$$\Delta H_{v,TS} = \Delta H_{v,b}\left[\frac{\left(1 - T_S / T_C\right)}{\left(1 - T_B / T_C\right)} \right]^n \qquad (24)$$

where:

$\Delta H_{v,TS}$	=	Enthalpy of vaporization at the average soil temperature, cal/mol
$\Delta H_{v,b}$	=	Enthalpy of vaporization at the normal boiling point, cal/mol
T_S	=	Average soil temperature, ^oK
T_C	=	Critical temperature, ^oK
T_B	=	Normal boiling point, ^oK
n	=	Exponent, unitless.

If data are not readily available for the average soil temperature, mean annual shallow soil temperature at depths of 100 cm or less can be estimated by [3]:

$$T_S = 4.646 + 0.986T_A \qquad (25)$$

where T_S is the mean annual soil temperature (°F) and T_A is the mean monthly air temperature (°F) for one or more years. The mean monthly air temperature is typically calculated from daily minimum and maximum temperatures obtained from a representative National Weather Service station. The standard error of estimate (S_{yx}) using Equation 25 is approximately 4.15°F. Seasonal estimates of average shallow soil temperature can be made using the following equations [3]:

$$\text{Summer}\, T_S = 16.115 + 0.856T_A;\ S_{yx} = 3.62°\ F \qquad (26)$$

$$\text{Fall}\, T_S = 1.578 + 1.023T_A;\ S_{yx} = 3.01°\ F \qquad (27)$$

(28)

(29)

The months of June, July, and August comprise the summer; September, October, and November, the fall; December, January, and February, the winter; and March, April, and May, the spring.

For depths greater than 100 cm, the mean annual soil temperature remains relatively stable throughout the year and can be estimated from the average shallow ground water temperatures shown in Figure 3-1.

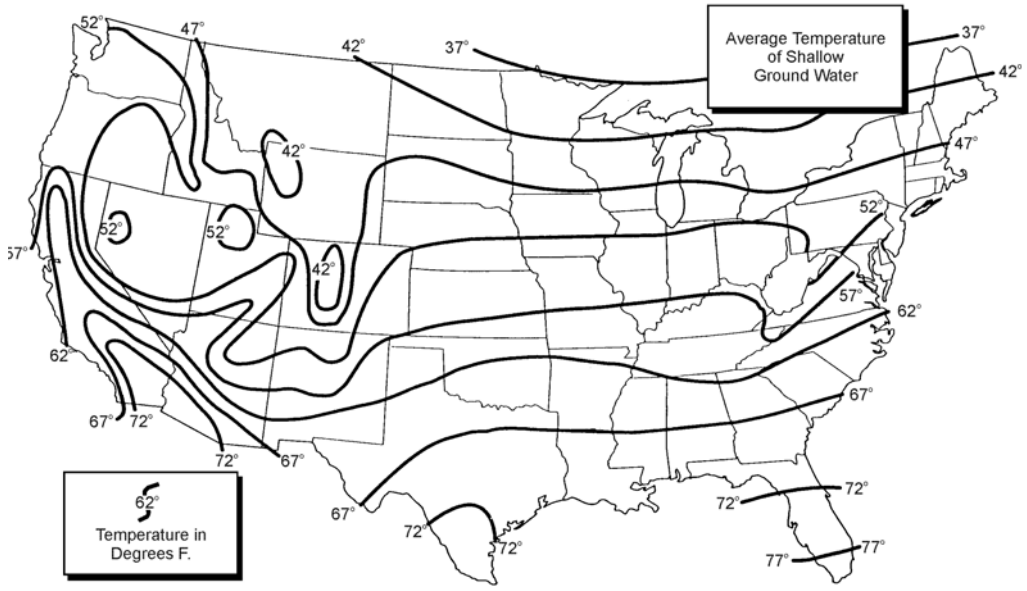


Figure 3-1. Average Shallow Ground Water Temperatures in the United States [4]

Table 3-1 gives the value of the exponent n in Equation 24 as a function of the ratio T_B/T_C.

Table 3-1. Values of Exponent n as a Function of T_B/T_C

Ratio T_B/T_C	Exponent n
< 0.57	0.30
0.57 – 0.71	0.74 (T_B/T_C) – 0.116
> 0.71	0.41

Chemical properties of many compounds such as the Henry's law constant (H_R), the normal boiling point (T_B), the critical temperature (T_C), and the enthalpy of vaporization at the normal boiling point ($\Delta H_{v,b}$) may be found in one or more of the following references:

- **CRC Handbook of Chemistry and Physics, 79th Ed.** 1998. CRC Press, Boca Raton, FA
- **Lange's Handbook of Chemistry, 15th Ed**. 1999. McGraw-Hill, New York, NY
- **Perry's Chemical Engineers' Handbook**, **7th Ed**. 1997. McGraw-Hill, New York, NY
- **Superfund Chemical Data Matrix**. U. S. EPA, Office of Emergency and Remedial Response, Washington, DC, EPA/540/R-96/028 *(http://www.epa.gov/oerrpage/superfund/resources/scdm/index.htm)*
- **Water9 PC-Based Expert Systems**. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC *(http://www.epa.gov/ttn/chief/software/water/index.html)*
- W.G. Mallard and P.J. Linstrom, Eds., **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**. November 1998. National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov/chemistry/)
- R. Sander. 1999. **Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Version 3** *(http://www.mpch-mainz.mpg.de/~sander/res/henry.html)*

The reader is reminded to use the correct chemical properties from the literature and to make any necessary units conversions. If the required properties cannot be found in the literature, general estimates of these values can be made with limited data. The critical temperature, for example, can be approximated from the normal boiling point by [2]:

$$T_C \approx 3T_B / 2 \tag{30}$$

The enthalpy of vaporization at the normal boiling point may also be approximated to within two significant figures by [2]:

$$\Delta H_{v,b} = \frac{2.303 B R_C T_B^2 \left(Z_g - Z_l\right)}{\left(t_b + C\right)^2} \tag{31}$$

where:

$\Delta H_{v,b}$	=	Enthalpy of vaporization at the normal boiling point, cal/mol
B	=	Antoine coefficient, °C
R_C	=	Gas constant (= 1.9872 cal/mol-°K)
T_B	=	Normal boiling point, °K
$(Z_g\text{-}Z_l)$	=	Compressibility factor difference, unitless (= 0.95 at T_B)
t_b	=	Normal boiling point, °C
C	=	Antoine coefficient, °C.

The Antoine coefficients *A* (not shown in Equation 31), *B*, and *C* are constants used to describe the vapor pressure curve of a volatile chemical as a function of temperature. As with the other chemical properties, Antoine coefficients may be found for many compounds in one or more of the references cited previously. If the Antoine coefficients are given in degrees Kelvin, the *C* coefficient should be converted to degrees Celsius by subtracting 273.15; the *B* coefficient, however, represents the slope of the curve and should not be converted. Care should also be taken to ensure that the value of the *B* coefficient listed in any reference does not already include a factor of 2.303 for converting base-10 to base-e logarithms. A simple method for determining whether this has been done is to check the value of *B* for methane. If the value is approximately 405.42 (°C or °K), the value may be used directly in Equation 31. If the value of *B* for methane is approximately 930°, the value has already been multiplied by 2.303.

If data are not available in the literature, the value of the Antoine *C* coefficient may be approximated from the normal boiling point using Table 3-2.

Table 3-2. Antoine Coefficient C for Organic Compounds

Boiling Point (°C)	C (°C)	Boiling Point (°C)	C (°C)
< -150	264 – 0.034 t_b	140	212
-150 to -10	240 – 0.19 t_b	160	206
-10	238	180	200
0	237	200	195
20	235	220	189
40	232	240	183
60	228	260	177
80	225	280	171
100	221	300	165
120	217		

For Polyhydric Alcohols (diols, triols, etc.): C = 230°C.

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The value of the Antoine *B* coefficient can also be estimated with a value of the *C* coefficient, the normal boiling point, and one pair of vapor pressure/temperature data [2]:

$$B = \frac{(t_b + C)(t_{Pv} + C)}{t_b - t_{Pv}} \log\left(\frac{760}{P_v}\right) \qquad (32)$$

where:
- B = Antoine coefficient, °C
- t_b = Normal boiling point, °C
- C = Antoine coefficient, °C
- t_{Pv} = Known temperature at vapor pressure P_v, °C
- 760 = Vapor pressure at the normal boiling point, mmHg
- P_v = Known vapor pressure at temperature t_{Pv}, mmHg.

Typically, literature values for vapor pressure (P_v) are at a temperature (t_{Pv}) of 20°C or 25°C. Combining this vapor pressure/temperature pair with that of the normal boiling point yields a linear approximation of the vapor pressure/temperature relationship. Although this relationship is not linear, the approximation given by Equation 32 requires only two pairs of data. Overall, use of Equation 32 will yield a maximum error of less than 50 percent.

Example Calculations

Estimate the dimensionless Henry's law constant for 1,3-Dichloropropene at a soil temperature of 10°C, given:

- Henry's law constant at 25°C = 1.77*E*-02 atm-m^3/mol
- Dimensionless Henry's law constant at 25°C = 7.26*E*-01
- Normal boiling point = 381.15°K or 108.00°C
- Vapor pressure at 25°C = 31.24 mmHg
- Critical temperature = 587.38°K.

1. From Table 3-2, the Antoine *C* coefficient is approximately 219°C.

2. From Equation 32, the Antoine *B* coefficient is:

$$B = \frac{(108 + 219)(25 + 219)}{108 - 25} \log\left(\frac{760}{31.24}\right)$$

$$B = 1{,}332° C.$$

3. From Equation 31, the enthalpy of vaporization at the normal boiling point within two significant figures is:

$$\Delta H_{v,b} = \frac{2.303 \times 1{,}332 \times 1.9872 \times 381.15^2 \times 0.95}{(108 + 219)^2}$$

$$\Delta H_{v,b} = 7{,}900 cal/mol.$$

4. From Equation 24, and Table 3-1, the enthalpy of vaporization at the soil temperature is:

$$\Delta H_{v,TS} = 7{,}900 \times \left[\frac{(1 - 283.15/587.38)}{(1 - 381.15/587.38)}\right]^{0.346}$$

$$\Delta H_{v,TS} = 9{,}100 cal/mol.$$

5. From Equation 23, the dimensionless Henry's law constant at the soil temperature is:

$$H'_{TS} = \frac{\exp\left[-\frac{9{,}100}{1.9872}\left(\frac{1}{283.15} - \frac{1}{298.15}\right)\right] \times 1.77E-02}{8.205E-05 \times 283.15}$$

$$H'_{TS} = 3.38E-01.$$

The enthalpy of vaporization at the normal boiling point ($\Delta H_{v,b}$) has been calculated using Equations 31 and 32 and Table 3-2 for 57 organic compounds. These values were then compared with the actual values of $\Delta H_{v,b}$ taken from the literature. Results indicated a maximum error of 29 percent, a minimum error of 0.5 percent, and a mean error of 5 percent. Finally, the value of the dimensionless Henry's law constant for each of the same 57 compounds was calculated at a soil temperature of 10°C. Equations 23 and 24 and Table 3-1 were used in these calculations; values of $\Delta H_{v,b}$ were taken from the literature. The values of the Henry's law constants at 10°C were then compared to their reference values at 25°C. Results indicated a maximum change in the value of the Henry's law constant of 90 percent and a minimum change of 30 percent. The largest changes occurred for the compounds with the highest boiling points and lowest vapor pressures.

Table 3-3 contains the chemical properties required to calculate the dimensionless Henry's law constant at the average soil temperature for the 93 volatile chemicals listed in the U.S. EPA 1996 *Soil Screening Guidance*.

Table 3-3 Chemical Properties of Selected Volatile SSL Chemicals

CAS No.	Chemical	Henry's Law Constant, H_R at 25 °C atm-m^3/mol	Normal Boiling Point, T_B °K	Normal Boiling Point, t_b °C	Critical Temperature, T_C °K	Vapor Pressure at 25 °C, P_v mmHg	Enthalpy of Vaporization at T_B, $\Delta H_{v,b}$ cal/mol	$\Delta H_{v,b}$ Ref.
50293	DDT	8.10E-06	533.15	260.00	720.75	3.93E-07	22,000	4
50328	Benzo(a)pyrene	1.13E-06	715.90	442.75	969.27	4.89E-09	19,000	4
51285	2,4-Dinitrophenol	4.44E-07	605.28	332.13	827.85	5.48E-03	25,000	3
53703	Dibenz(a,h)anthracene	1.47E-08	743.24	470.09	990.41	2.05E-11	29,995	3
56235	Carbon tetrachloride	3.05E-02	349.90	76.75	556.60	1.12E+02	7,127	1
56553	Benz(a)anthracene	3.34E-06	708.15	435.00	1,004.79	1.54E-07	16,000	4
57749	Chlordane	4.85E-05	624.24	351.09	885.73	2.70E-05	14,000	4
58899	gamma-HCH (Lindane)	1.40E-05	596.55	323.40	839.36	3.72E-05	15,000	4
60571	Dieldrin	1.51E-05	613.32	340.17	842.25	9.96E-07	17,000	4
65850	Benzoic Acid	1.54E-06	720.00	446.85	751.00	6.51E-03	12,094	3
67641	Acetone	3.88E-05	329.20	56.05	508.10	2.27E+02	6,955	1
67663	Chloroform	3.66E-03	334.32	61.17	536.40	2.04E+02	6,988	1
67721	Hexachloroethane	3.88E-03	458.00	184.85	695.00	4.72E-01	9,510	2
71363	Butanol	8.80E-06	390.88	117.73	563.05	6.54E+00	10,346	1
71432	Benzene	5.56E-03	353.24	80.09	562.16	9.50E+01	7,342	1
71556	1,1,1-Trichloroethane	1.72E-02	347.24	74.09	545.00	1.24E+02	7,136	1
72208	Endrin	7.51E-06	718.15	445.00	986.20	5.84E-07	15,000	4
72435	Methoxychlor	1.58E-05	651.02	377.87	848.49	1.23E-06	16,000	4
72548	DDD	4.00E-06	639.90	366.75	863.77	8.66E-07	17,000	4
72559	DDE	2.10E-05	636.44	363.29	860.38	5.66E-06	15,000	4
74839	Methyl bromide	6.24E-03	276.71	3.56	467.00	1.64E+03	5,714	1
75014	Vinyl chloride (chloroethene)	2.71E-02	259.25	-13.90	432.00	2.80E+03	5,250	2
75092	Methylene chloride	2.19E-03	313.00	39.85	510.00	3.70E+02	6,706	1
75150	Carbon disulfide	3.02E-02	319.00	45.85	552.00	3.40E+02	6,391	1
75252	Bromoform	5.34E-04	422.35	149.20	696.00	5.94E+00	9,479	1
75274	Bromodichloromethane	1.60E-03	363.15	90.00	585.85	5.84E+01	7,800	4
75343	1,1-Dichloroethane	5.61E-03	330.55	57.40	523.00	2.28E+02	6,895	1
75354	1,1-Dichloroethylene	2.61E-02	304.75	31.60	576.05	5.99E+02	6,247	1
76448	Heptachlor	1.09E-03	603.69	330.54	846.31	3.26E-04	13,000	4
77474	Hexachlorocyclopentadiene	2.71E-02	512.15	239.00	746.00	7.32E-02	10,931	2
78591	Isophorone	6.63E-06	488.35	215.20	715.00	4.09E-01	10,271	2
78875	1,2-Dichloropropane	2.80E-03	369.52	96.37	572.00	5.06E+01	7,590	2
79005	1,1,2-Trichloroethane	9.12E-04	386.15	113.00	602.00	2.52E+01	8,322	1
79016	Trichloroethylene	1.03E-02	360.36	87.21	544.20	7.20E+01	7,505	1
79345	1,1,2,2-Tetrachloroethane	3.44E-04	419.60	146.45	661.15	5.17E+00	8,996	1
83329	Acenaphthene	1.55E-04	550.54	277.39	803.15	3.75E-03	12,155	2
84662	Diethylphthalate	4.51E-07	567.15	294.00	757.00	1.65E-03	13,733	2
84742	Di-n-butyl phthalate	9.39E-10	613.15	340.00	798.67	4.22E-05	14,751	1

Table 3-3 Chemical Properties of Selected volatile SSL Chemicals

CAS No.	Chemical	Henry's Law Constant, H_R at 25 °C atm-m^3/mol	Normal Boiling Point, T_B °K	Normal Boiling Point, t_b °C	Critical Temperature, T_C °K	Vapor Pressure at 25 °C, P_v mmHg	Enthalpy of Vaporization at T_B, $\Delta H_{v,b}$ cal/mol	$\Delta H_{v,b}$ Ref.
85687	Butyl benzyl phthalate	1.26E-06	660.60	387.45	839.68	1.20E-05	14,000	4
86306	N-Nitrosodiphenylamine	5.00E-06	632.28	359.13	890.45	1.00E-01	7,300	4
86737	Fluorene	6.37E-05	570.44	297.29	870.00	6.21E-04	12,666	2
86748	Carbazole	1.53E-08	627.87	354.72	899.00	2.66E-04	13,977	2
87683	Hexachloro-1,3-butadiene	8.15E-03	486.15	213.00	738.00	1.77E-01	10,206	2
87865	Pentachlorophenol	2.44E-08	582.15	309.00	813.20	5.40E-04	16,109	3
88062	2,4,6-Trichlorophenol	7.78E-06	519.15	246.00	749.03	1.18E-02	12,000	4
91203	Naphthalene	4.83E-04	491.14	217.99	748.40	8.89E-02	10,373	2
91941	3,3-Dichlorobenzidine	4.00E-09	560.26	287.11	754.03	2.20E-07	20,000	4
95476	o-Xylene	5.20E-03	417.60	144.45	630.30	6.60E+00	8,661	1
95487	2-Methylphenol (o-cresol)	1.20E-06	464.19	191.04	697.60	3.16E-01	10,800	1
95501	1,2-Dichlorobenzene	1.90E-03	453.57	180.42	705.00	1.36E+00	9,700	2
95578	2-Chlorophenol	3.90E-04	447.53	174.38	675.00	2.11E+00	9,572	2
95954	2,4,5-Trichlorophenol	4.34E-06	526.15	253.00	759.13	1.63E-02	11,000	4
98953	Nitrobenzene	2.40E-05	483.95	210.80	719.00	2.44E-01	10,566	2
100414	Ethylbenzene	7.88E-03	409.34	136.19	617.20	9.58E+00	8,501	1
100425	Styrene	2.76E-03	418.31	145.16	636.00	6.24E+00	8,737	2
105679	2,4-Dimethylphenol	2.00E-06	484.13	210.98	707.60	1.26E-01	11,329	2
106423	p-Xylene	7.66E-03	411.52	138.37	616.20	8.89E+00	8,525	1
106467	1,4-Dichlorobenzene	2.43E-03	447.21	174.06	684.75	1.06E+00	9,271	2
106478	p-Chloroaniline	3.32E-07	503.65	230.50	754.00	2.35E-02	11,689	2
107062	1,2-Dichloroethane	9.78E-04	356.65	83.50	561.00	8.13E+01	7,643	1
108054	Vinyl acetate	5.12E-04	345.65	72.50	519.13	1.09E+02	7,800	2
108383	m-Xylene	7.34E-03	412.27	139.12	617.05	8.51E+00	8,523	1
108883	Toluene	6.63E-03	383.78	110.63	591.79	2.82E+01	7,930	1
108907	Chlorobenzene	3.71E-03	404.87	131.72	632.40	1.21E+01	8,410	1
108952	Phenol	3.98E-07	455.02	181.87	694.20	4.36E-01	10,920	1
111444	Bis(2-chloroethyl)ether	1.80E-05	451.15	178.00	659.79	1.34E+00	10,803	3
115297	Endosulfan	1.12E-05	674.43	401.28	942.94	9.96E-06	14,000	4
117817	Bis(2-ethylhexyl)phthalate	1.02E-07	657.15	384.00	806.00	6.45E-06	15,999	2
117840	Di-n-octyl phthalate	6.68E-05	704.09	430.94	862.22	4.47E-06	14,000	4
118741	Hexachlorobenzene	1.32E-03	582.55	309.40	825.00	1.23E-05	14,447	2
120127	Anthracene	6.51E-05	615.18	342.03	873.00	2.55E-05	13,121	2
120821	1,2,4-Trichlorobenzene	1.42E-03	486.15	213.00	725.00	3.36E-01	10,471	2
120832	2,4-Dichlorophenol	3.17E-06	482.15	209.00	708.17	5.48E-03	15,000	4
121142	2,4-Dinitrotoluene	9.27E-08	590.00	316.85	814.00	1.74E-04	13,467	2
124481	Chlorodibromomethane	7.83E-04	416.14	142.99	678.20	3.12E+01	5,900	4
127184	Tetrachloroethylene	1.84E-02	394.40	121.25	620.20	1.84E+01	8,288	1

Table 3-3 Chemical Properties of Selected Volatile Chemicals

CAS No.	Chemical	Henry's Law Constant, H_R at 25 °C atm-m^3/mol	Normal Boiling Point, T_B °K	Normal Boiling Point, t_b °C	Critical Temperature, T_C °K	Vapor Pressure at 25 °C, P_v mmHg	Enthalpy of Vaporization at T_B, $\Delta H_{v,b}$ cal/mol	$\Delta H_{v,b}$ Ref.
129000	Pyrene	1.10E-05	667.95	394.80	936.00	4.25E-06	14,370	2
156592	cis-1,2-Dichloroethylene	4.07E-03	333.65	60.50	544.00	1.75E+02	7,192	2
156605	trans-1,2-Dichloroethylene	9.39E-03	320.85	47.70	516.50	3.52E+02	6,717	2
193395	Indeno(1,2,3-cd)pyrene	1.60E-06	809.15	536.00	1,078.24	1.43E-10	19,000	4
205992	Benzo(b)fluoranthene	1.11E-04	715.90	442.75	969.27	8.06E-08	17,000	4
206440	Fluoranthene	1.61E-05	655.95	382.80	905.00	8.13E-06	13,815	2
207089	Benzo(k)fluoranthene	8.29E-07	753.15	480.00	1,019.70	2.00E-09	18,000	4
218019	Chrysene	9.46E-05	714.15	441.00	979.00	7.83E-09	16,455	2
309002	Aldrin	1.70E-04	603.01	329.86	839.37	1.67E-05	15,000	4
319846	alpha-HCH (alpha-BHC)	1.06E-05	596.55	323.40	839.36	4.26E-05	15,000	4
319857	beta-HCH (beta-BHC)	7.44E-07	596.55	323.40	839.36	4.90E-07	19,000	4
542756	1,3-Dichloropropene	1.77E-02	381.15	108.00	587.38	3.12E+01	7,900	4
606202	2,6-Dinitrotoluene	7.46E-07	558.00	284.85	770.00	5.68E-04	12,938	2
621647	N-Nitrosodi-n-propylamine	2.25E-06	509.60	236.45	746.87	3.52E+00	6,100	4
1024573	Heptachlor epoxide	9.51E-06	613.96	340.81	848.76	4.34E-06	16,000	4
7439976	Mercury (elemental)	1.14E-02	629.88	356.73	1,750.00	2.00E-03	14,127	1
8001352	Toxaphene	6.00E-06	657.15	384.00	873.31	4.19E-06	15,000	4

1 – CRC Handbook of Chemistry and Physics, CRC Press (1994).

2 – Design Institute for Physical Property Data, The American Institute for Chemical Engineers, on-line data search, 1997.

3 – Lange's Handbook of Chemistry 15th Ed., McGraw-Hill (1999).

4 - $\Delta H_{v,b}$ calculated from boiling point and vapor pressure using Equations and Tables in this guidance.

Air Diffusion Coefficient and Aqueous Diffusion Coefficient--

Diffusion is the process by which a chemical moves in the direction of its concentration gradient due to the random motion of individual molecules. Based on a review of existing values for organic compounds of intermediate molecular weight, Jury et al. (1983) concluded that the air diffusion coefficients and aqueous diffusion coefficients vary very little for different pesticides. Therefore, they used a default value of 4,320 cm^2/day for the air diffusion coefficient and a default value of 0.432 cm^2/day for the aqueous diffusion coefficient in their analyses. In the absence of measurements in the available literature, these values can also be estimated according to methods presented in Lyman et al. (1990). Diffusion coefficients for EMSOFT must be specified in units of cm^2/day.

Air diffusion and aqueous diffusion coefficients for many volatile organic compounds (VOCs) can be found in U.S. EPA (1996). In addition, they may be calculated using the U.S. EPA PC-based computer codes CHEMDAT8 or WATER8 which may be accessed free of charge from the U.S. EPA Office of Air Quality Planning and Standards (OAQPS) Technology Transfer Network (TTN) bulletin board.

Half Life--

The half life ($t_{1/2}$) of a chemical is a measure of its persistence in a given medium (e.g., soil, ground water, surface water, etc.). More precisely, it is the time it takes for half of a given mass of chemical to decay (by any number of processes, including biodegradation, photolysis, and oxidation). Assuming a first-order decay process, chemical concentration would decrease according to the following equation:

$$C = C_0 \exp(-\mu t) \tag{33}$$

where C is the concentration at time t, C_o is the initial concentration, and μ is the decay constant, equal to ln $2/t_{1/2}$. In this model, half life must be given in days. Measured half lives can vary significantly for a given chemical due to differences in soil conditions and microbial populations; thus, the user should choose this value carefully or conservatively, and examine the influence of the chosen half life value on the overall model results.

Literature values for half life or degradation rate are typically laboratory values or derived from laboratory values and may not be applicable to site-specific conditions. For this reason, degradation and transformation should be disregarded unless site-specific decay constants can be determined. Degradation in EMSOFT may be disregarded in the system calculations by setting the value of the half life to 1,000,000 days.

Table 3-4 gives the range of acceptable values for the chemical data when running the EMSOFT model. Values entered outside of these ranges will result in an error message, which will prompt the user to re-enter that data within the specified range.

TABLE 3-4. VALUE RANGES FOR CHEMICAL DATA

Chemical parameter	Units	Acceptable range
Organic carbon partition coefficient	ml/g	1.00E-2 to 1.00E+9
Henry's law constant	(dimensionless)	1.00E-1 to 1.00E+3
Air diffusion coefficient	(cm^2/day)	1.00E+1 to 1.00E+5
Aqueous diffusion coefficient	(cm^2/day)	1.00E-2 to 1.00E+1
Half life	(days)	0 to 1.00E+6

Once all the chemical data are entered, the data set may be saved by pressing the button labeled "Save chemical data...". This will open a save chemical data dialog box. To save the values, the user must specify a file name in the field labeled "File Name:". It should be noted that it is not necessary to enter a file extension as the program automatically does this for the user. If the user, however, does enter an extension the result will be a file with a double extension (e.g., filename.extension.ECF). Once the file has been named, the user must press the SAVE button. This will return the designated path and file name to the field on the right of the "Save Chemical Data..." button.

3.4.5 Screen 5: Soil Properties and Physical Constants

Soil properties are entered in this screen along with two model constants: the rate at which porewater moves upward or downward within the soil, and the atmospheric boundary layer thickness. These model inputs are described briefly below.

Fraction Organic Carbon--

The fraction organic carbon (f_{oc}) is the fraction of the soil, on a dry weight basis, that is organic carbon. This parameter is typically measured for a site from soil samples. In the absence of site-specific data, a conservatively low value could be used (i.e., one that would result in less sorption and therefore greater volatilization). A low organic carbon fraction, representative of a soil with very little organic material, would be on the order of 0.005 or less, while a high organic carbon fraction, representative of soils with significant organic material, could be as high as 0.01.

Porosity--

Soil porosity (φ) is equal to the volume of pore space within a soil sample divided by the total volume of the sample. It is usually measured from soil samples collected at a site. Porosity values for natural soils range from 0.20 for a glacial till to 0.75 for a very organic clay. Porosities for sands typically range between 0.25 and 0.50, silts between 0.35 and 0.50, and clays between 0.40 and 0.70 (Freeze and Cherry, 1979).

Water Content--

The water content (θ) is equal to the ratio of the volume of water in a sample to the total volume of a sample. Under unsaturated conditions, it is less than the soil porosity. Water content is commonly measured from soil samples collected at a site. Coarse-grained soils usually have a lower water content than finer-grained soils. Sands, for example, tend to have water contents less than 0.20 while silty and other fine-grained soils will have water contents between 0.35 and 0.45 (Jury, undated). If long simulation time periods are desired, long-term average water contents should be estimated.

Bulk Density--

The bulk density (ρ_b) is equal to the dry weight of a soil sample divided by the soil sample volume. It can be measured from soil samples collected in the field. Alternatively, it can be calculated as (1-n) times the specific gravity of the soil solids. The specific gravity for many common soil minerals is between 2.6 and 2.8 (Dunn et al., 1980). Thus, for a porosity range of 0.30 to 0.50 and a specific gravity of 2.7, the bulk density ranges from 1.35 to 1.9 g/cm^3.

Porewater Flux–

The porewater flux (J_w) is assumed to be constant in the model, despite the highly variable nature of porewater movement both upward and downward in the unsaturated zone under field conditions. (This assumption is necessary to allow for an analytical solution to the governing equations.) Upward movement of porewater (evaporation) might be induced under conditions of low atmospheric humidity and solar heating of the soil. Downward movement of porewater would be caused by infiltration of precipitation or irrigation water.

Due to the high degree of uncertainty associated with this variable, and the sensitivity of model results to its magnitude, it will usually be necessary to use a conservative value for the porewater flux. A positive value indicates a downward porewater flux and a negative value indicates an upward porewater flux. An upward flux will result in greater volatilization rates. The model units for this parameter are cm/day.

On an annual average basis, the porewater flux is typically represented by the annual ground water recharge rate. (Except in extremely arid climates, there is generally a net downward movement of water). The ground water recharge rate depends on a complex relationship between a number of parameters that describe the climate and soil properties at a particular location. Computer models are available to perform these calculations, including SESOIL (Bonazountas and Wagner, 1984), and the HELP (Hydrologic Evaluation of Landfill Performance) model (Schroeder, 1989).

Alternatively, recharge estimates by hydrogeologic setting may be obtained from Aller et al. (1987). When using the Aller et al. (1987) estimates, the user should recognize that site-specific values may differ to some extent. For example, areas within the setting with steeper than average slopes will tend to have lower infiltration rates while areas with flatter than average slopes or depressions will tend to have higher infiltration rates. If no data are available, it would be conservative for the purpose of calculating long-term volatilization rates and soil concentrations to assume a porewater flux of zero.

If short-term emission rates are of interest, it might be more appropriate to assign a porewater flux based on the capillary rise of ground water, which is the primary means of groundwater transport to the surface during the dry season. Eagleson (1978) presents the following equation to calculate this evaporation rate:

$$E = K_{sat}\left[1 + \frac{3/2}{mc\ 1}\right]\left[\frac{\psi_{sat}}{Z}\right]^{mc} \quad for \quad \frac{E}{E_{pot}} < 1 \tag{34}$$

where K_{sat} = Saturated hydraulic conductivity (cm/s)

m = Pore size distribution index

c = Pore disconnectedness index

ψ_{sat} = Saturated soil matrix potential (cm)

Z = Depth to water table (cm)

E_{pot} = Potential evapotranspiration.

The parameter m is calculated from the following relationship:

$$m = \frac{2}{c\ 3} \tag{35}$$

Guidance on the selection of c is provided by Table 3-5. Guidance on the selection of representative soil hydraulic parameters is provided by Table 3-6.

TABLE 3-5. VALUES OF PORE DISCONNECTEDNESS INDEX (c) FOR VARIOUS SOIL TYPES

Soil type	c
Clay	12
Clay loam	10
Silty loam	5
Sandy loam	4
Source: Eagleson, 1977, as cited in Bonazoutas and Wagner, 1984	

TABLE 3-6. REPRESENTATIVE VALUES OF SOIL HYDRAULIC PARAMETERS

Soil texture	K_{sat}, cm/min	Ψ_{sat}, cm
Sand	1.056	12.1 (14.3)[1]
Loamy sand	0.938	9.0 (12.4)
Sandy loam	0.208	21.8 (31.0)
Silt loam	0.0432	78.6 (51.2)
Loam	0.0417	47.8 (51.2)
Sandy clay loam	0.0378	29.9 (37.8)
Silty clay loam	0.0102	35.6 (37.8)
Clay loam	0.0147	63.0 (51.0)
Sandy clay	0.0130	15.3 (17.3)
Silty clay	0.0062	49.0 (62.1)
Clay	0.0077	40.5 (39.7)

Source: Clapp and Homeberger, 1978
[1]Standard deviation in parentheses.

The potential evapotranspiration rate represents the maximum upward porewater flux that would be possible, given an unlimited supply of water in the soil. It is therefore the upper bound to the upward porewater flux, and would therefore represent an extremely conservative value. The modified Penman energy balance equation can be used to estimate the average rate of potential evapotranspiration (Eagleson, 1977, as cited in Bonazountas and Wagner, 1984). This equation is not presented here due to its complicated formulation. The interested reader should consult the cited references for further information. As an indication of the feasible range of potential evapotranspiration rates, measured values are provided in Table 3-7.

Boundary Layer Thickness--

The atmospheric boundary layer thickness at the soil surface can be calculated from the following equation (Jury, 1983):

$$d = \frac{D_{wv}^{air} \rho_{wv} (1 - RH)}{2E\rho_{WL}} \tag{36}$$

TABLE 3-7. OBSERVED VALUES OF ANNUAL POTENTIAL EVAPORTRANSPIRATION

Location	Observed E_{pot}, in/yr
Mesilla, N.M.	34.0
Pecos, N.M.	35.3
Sangamon R., III.	29.2
Green R., Ky.	31.4
Tellapoosa R., GA.	33.0
Mad R., Ohio	25.8
Skunk R., Iowa	27.0
W. Ford, White R., Mo.	31.0
N. Platte R., Neb.	23.8
Black R., Wis.	22.2
Cyprus Crk., Tex.	36.2
Wagon Wheel Gap., Col.	15.6
Merrimac R., Ma.	21.5
West R., Vt.	21.5
Swift R., Ma.	23.1
Source: P. Eagleson (1977), as cited in Bonazountas and Wagner (1984)	

where D_{wv}^{air} = Binary diffusion coefficient of water vapor in air

ρ_{wv} = Saturated water vapor density

RH = Relative humidity

E = Evaporation rate

ρ_{WL} = Density of liquid water.

D_{wv}^{air} is equal to approximately 2 m^2/day. This equation can be used in cases where the upward porewater flux is nonzero.

An alternative equation, which takes into account windspeed, is (Thibodeaux, 1981):

$$d = \frac{26\nu}{VSc^{1/3}} \tag{37}$$

where ν = Kinematic viscosity of air (about 1.5×10^{-5} m^2/s)

V_* = Friction velocity

Sc = Schmidt number.

The friction velocity (in units of m/s) can be calculated from the following equation (EPA, 1987):

$$V = 0.01V\left(6.1 + 0.63V\right)^{0.5} \tag{38}$$

where V is the ambient windspeed in m/s. The Schmidt number is equal to D_G^{air}/ν.

Typical values for boundary layer thickness were calculated using Equations 37 and 38 with a range of windspeeds. These calculations are summarized in Table 3-8, which shows boundary layer thickness ranging from 0.13 cm to 1.8 cm for VOCs and 0.16 cm to 2.2 cm for PCB.

TABLE 3-8. BOUNDARY LAYER THICKNESSES FOR DIFFERENT WINDSPEEDS

	Boundary layer thickness, cm	
Windspeed, m/s	VOCs[1]	PCB[2]
1	1.81	2.16
5	0.31	0.37
10	0.13	0.16

[1]Average $D_G^{air} = 0.085$ cm^2/s; D_G^{air} values range from 0.06 to 0.11 cm^2/s for common VOCs.
[2]$D_G^{air} = 0.05$ cm^2/s.

Table 3-9 presents boundary layer thicknesses calculated from laboratory and field experiments by Jury et al. (1984c). They are of the same magnitude as those calculated from Equations 37 and 38. Calculations by Jury et al. (1984c) using Equation 36 are also in general

agreement with the values shown in Table 3-9. A default boundary layer thickness that may be used in EMSOFT when no other data are available is 0.5 cm.

TABLE 3-9. BOUNDARY LAYER THICKNESSES CALCULATED FROM LABORATORY AND FIELD EXPERIMENTS

Compound	Experiment	d, cm	Comments
Trifluralin	Field	0.84	Windspeed 2.0 - 2.7 m/s
Heptachlor	Field	1.30	
Dacthal	Field	0.68	
Chlordane	Field	0.88	
Average = 0.93			
Trifluralin	Field	0.16	Windspeed 3.8 - 5.8 m/s
Lindane	Field	0.13	
Average = 0.15			
Triallate	Lab	0.37	50% relative humidity
Triallate	Lab	0.21	
Average = 0.28			
Trifluralin	Lab	0.39	100% relative humidity
Lindane	Lab	0.12	50-100% cycled relative humidity
Dieldrin	Lab	0.78	50% relative humidity
Source: Jury et at., 1984c			

Table 3-10 gives the range of acceptable values for the soil properties and physical constants when running the EMSOFT model. Values entered outside of these ranges will result in a system error.

TABLE 3-10. VALUE RANGES FOR SOIL PROPERTIES AND PHYSICAL CONSTANTS

Parameter	Units	Acceptable range
Soil organic carbon	Fraction	0.0 - 1.0
Soil porosity	dimensionless	0.05 - 0.70
Soil water content	dimensionless	0.0 - 0.70
Soil bulk density	g/cm^3	0.5 - 5.0
Porewater flux	cm/day	-1.0 - 1.0
Boundary layer thickness	cm	0.01 - 10.0

3.4.6 Screen 6: Layer Properties

The cover thickness and the thickness and concentration of contaminated soil layers are specified in this screen. The cover is assumed to be an uncontaminated soil layer at the surface. If contamination begins at the surface, a value of 0.0 should be assigned to the cover thickness. The number of contaminated layers for which input is requested (maximum of 10) will correspond to the number specified in Screen 4 (chemical data). Layer thicknesses must be given in cm and concentrations in mg/kg. All input fields must be filled before continuing.

3.4.7 Screen 7: Input/Output Save

The full set of input parameter values and output values can be saved to document a model run, preserve input parameters for future use, and allow for analysis and graphing of results. As in the other input screens, these parameters and results can be saved by pressing the buttons on the left labeled “Save Input...” and “Save Output...” Similar dialogs will appear as when saving the chemical data. It should be noted again that the program will assign the proper file extension, and this should not be performed by the user. The saved input data file will be given a .DAT file extension and the output file will be given a .OUT file extension. Upon acceptance of the selections and file names entered on this screen, the model will commence calculations.

3.4.8 Screen 8: Calculating ...

This screen displays a message instructing the user to wait while the model is performing calculations. No action is required. When the calculations are completed, control is automatically transferred to the next screen.

3.4.9 Screen 9: Flux Results

Upon completion of calculations, the model displays flux results for the calculation options selected. The user can scroll through the flux versus time results using scroll bars or by clicking within the data box and using the up and down arrow keys. The page up and page down keys can also be used.

3.4.10 Screen 10: Soil Concentration Results

This screen displays the soil concentration results. Two scroll regions are active in this screen, one for the soil concentration versus depth and the other for depth-averaged soil concentration versus time. The depth- and time-averaged soil concentration is displayed in the right side of the screen, along with the depth and time used for averaging. The time displayed also represents the time corresponding to the concentration-versus-depth results. At this point, the user has the option of returning to the previous screen of flux results or continuing to the print results screen.

3.4.11 Screen 11: Print Results

This screen gives the user the ability to print the results of the model run. The user will be asked "Would you like to print your EMSOFT modeling results?" By pressing the YES button the results will be sent to the default selected printer. EMSOFT sends print spooling through the LPT1 port, which is the default printer port.

IMPORTANT NOTE: If you are printing through a network connected printer, it may be necessary to capture the LPT1 port for that printer. Please refer to your Windows help or contact your network administrator should this be needed.

To continue without printing press the NO button. Once printed or the NO button is pressed, the final screen will be displayed.

3.4.12 Screen 12: Restart/Quit

In this final screen, the user is given the option of returning to the beginning of the model (Screen No. 2) to run the simulation for a new set of input parameters. Otherwise, the "NO, EXIT" option can be selected to terminate execution of the model. To restart the model, press the YES, RESTART button. Unlike the previous version, the newly created data files are accessible upon restart. Also, all previously input data will be retained.

SECTION 4

MODEL VERIFICATION

The fate of benzene in a sandy and in a clayey soil was simulated to verify the results of EMSOFT. For comparison, the model SCREENB (developed by Jury (undated)) was used to simulate the fate of benzene under the same soil conditions. Chemical properties, soil properties, layer properties, and other model input parameters were taken from examples presented by Jury et al. (1990). Plots of surface volatilization flux versus time and soil concentration versus depth from each model were then compared against similar plots shown in Figure 1 of Jury et al. (1990). Chemical and soil property data and layer data, taken directly from Tables 1 and 2 of Jury et al. (1990), are reproduced below.

Chemical Properties for Benzene

Organic carbon partition coefficient	80 ml/g
Dimensionless Henry's Law constant	0.22
First-order degradation half life	365 days
Free-air diffusion coefficient	4,320 cm^2/day
Free-water diffusion coefficient	0.432 cm^2/day

Soil Properties

	Sandy soil	Clayey soil
Fractional organic carbon	0.0075	0.025
Total porosity	0.40	0.50
Water-filled porosity	0.18	0.375
Bulk density (g/cm^3)	1.59	1.32
Pore Water Flux (cm/day)	0	0

Layer Properties

Number of layers	1
Simulation depth (cm)	300
Simulation time (days)	365

Evaporation rate (cm/day)	0
Boundary layer thickness (cm)	0.5
Depth to contaminated layer (cm)	100
Thickness of contaminated layer (cm)	30
Initial concentration ($\mu g/cm^3$)	25 (equal to 15.72 mg/kg sand, 18.94 mg/kg clay)

As the first step in model verification, simulation results between the two models were compared. The surface volatilization fluxes from EMSOFT and SCREENB are depicted in Figures 4-1 and 4-2, respectively, while the vertical concentration profiles simulated by each model appear in Figures 4-3 and 4-4, respectively. Comparison of Figures 4-1 and 4-2 showed that the volatilization fluxes simulated by the models agreed for the case of the sandy soil; results of the model for the case of the clayey soil did not, however, agree. Vertical concentration profiles generated by each model were the same for each soil.

Model results were then compared against the data graphed in Figure 1 of Jury et al. (1990). The comparison between the models' output and Figure 1 of Jury et al. (1990) was facilitated by plotting the vertical concentration profile and surface flux results for each model at the same dimensions, units, and increments as the plots shown in Figure 1 of Jury et al. (1990). This comparison is shown in Figure 4-5. Results from EMSOFT agreed with Jury et al. (1990) for volatilization flux and vertical concentration for both soil types. From SCREENB, surface flux results from the clayey soil failed to agree with the results from Jury et al. (1990).

In conclusion, EMSOFT reproduced the simulation results for surface flux and vertical concentration of benzene in sandy and clayey soils reported in Jury et al. (1990). The vertical concentration results from SCREENB agreed with EMSOFT results and with Jury et al. (1990) for both soils. The surface volatilization flux results from SCREENB did not agree with the results for the clayey soil from EMSOFT and Jury et al. (1990).

The surface volatilization fluxes from the sandy soil for each model agreed with Jury et al. (1990); only the surface volatilization flux from the clayey soil simulated by EMSOFT, however, reproduced the flux plotted in Figure 1 of Jury et al. (1990). Both models produced the same vertical concentration results as those shown in Figure 1 of Jury et al. (1990).

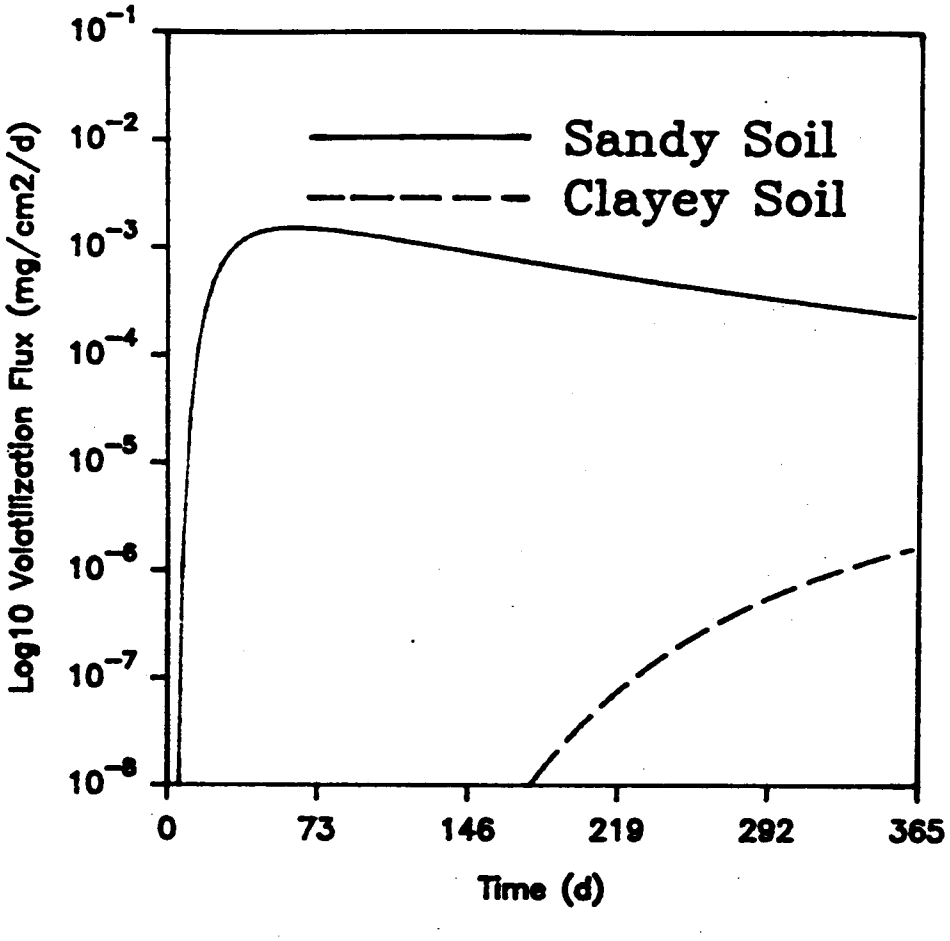

Figure 4-1. Flux versus time for benzene calculated by EMSOFT.

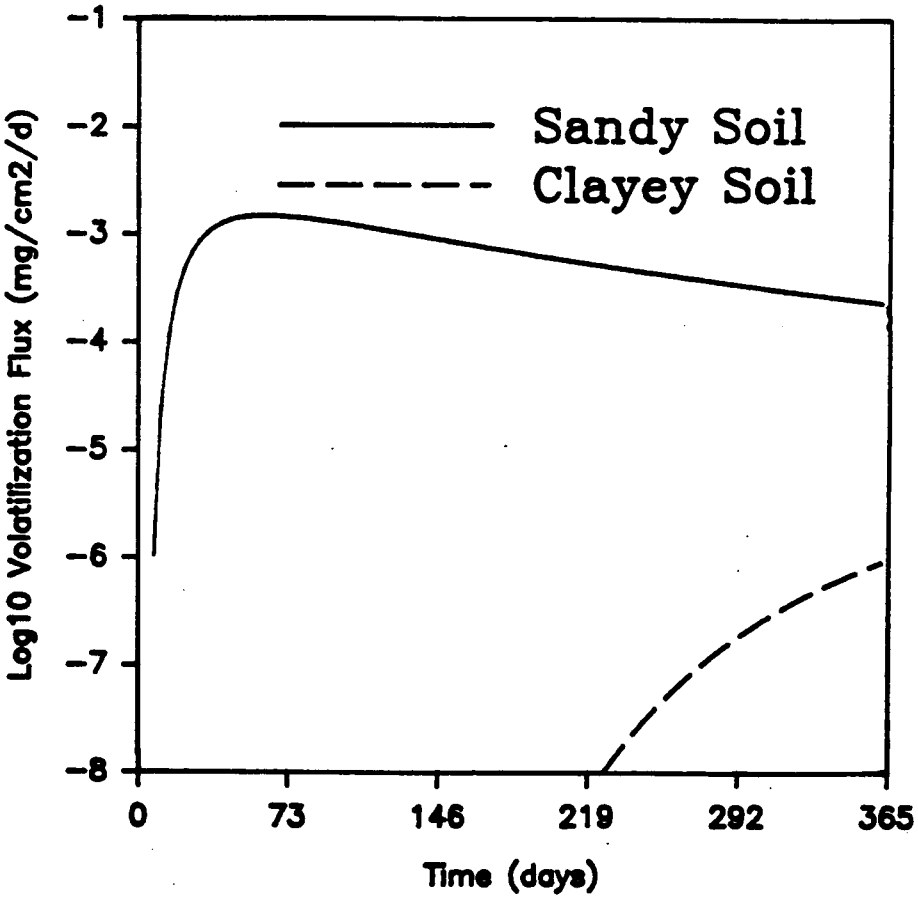

Figure 4-2. Flux versus time for benzene calculated by SCREENB.

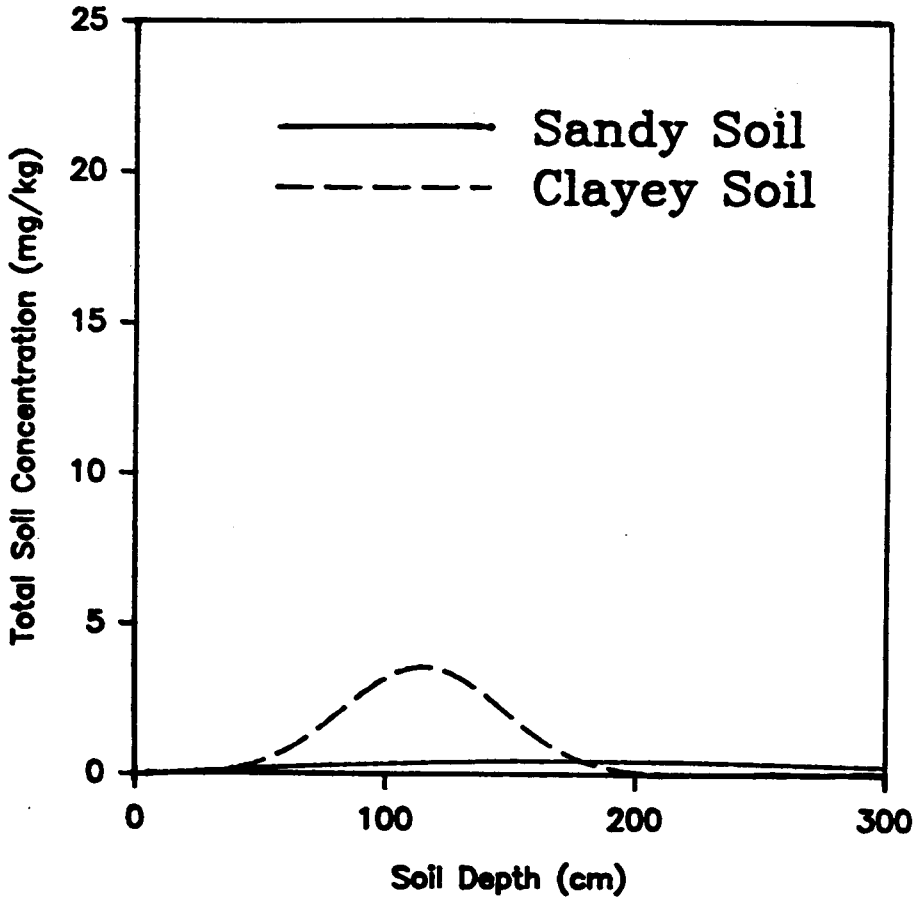

Figure 4-3. Concentration versus depth for benzene calculated by EMSOFT.

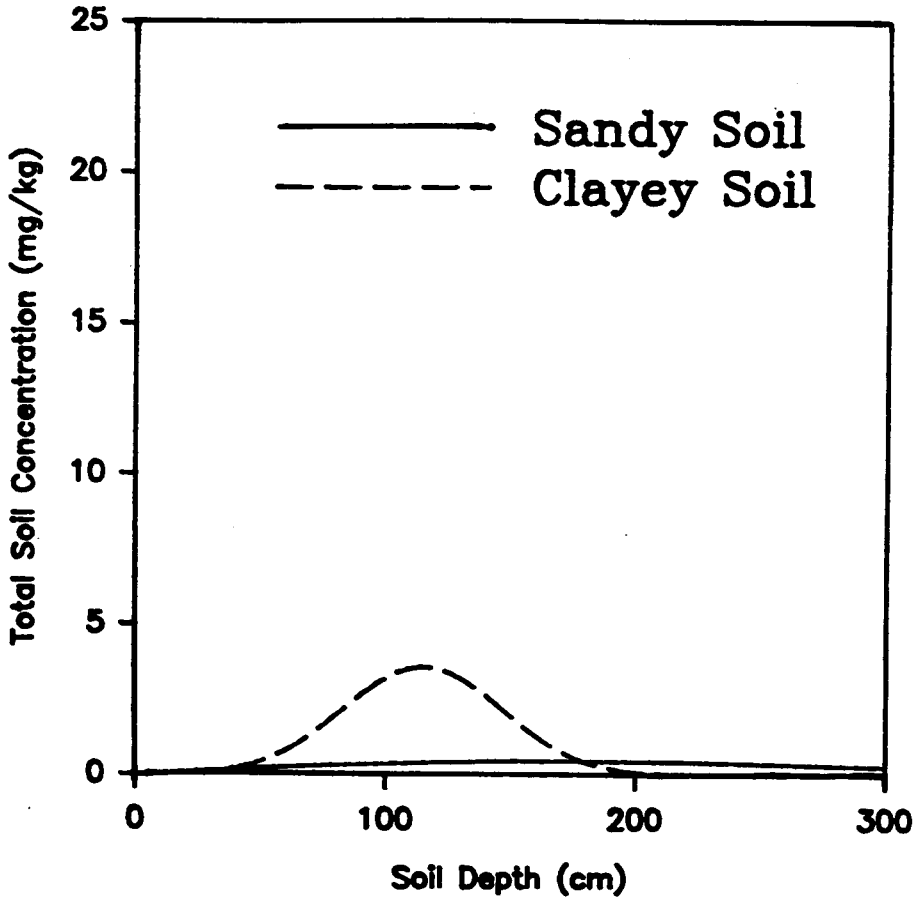

Figure 4-4. Concentration versus depth for benzene calculated by SCREENB.

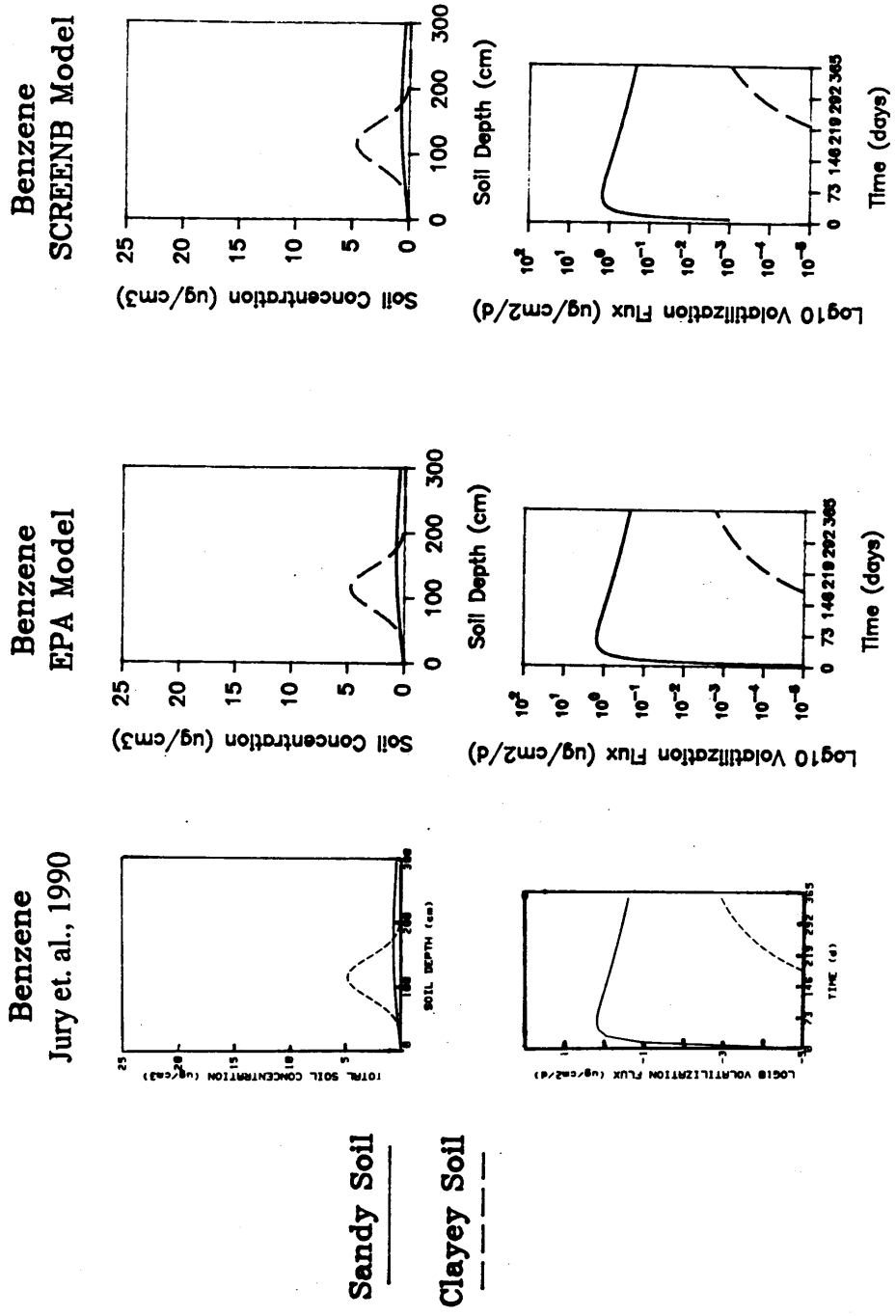

Figure 4-5. Comparison of surface flux and concentration results from Jury et al (1990).

SECTION 5

VALIDATION

This section presents a limited validation analysis of the EMSOFT model. For this exercise, data sets were selected from the scientific literature which contained measurements of air emissions of organic compounds from contaminated soils. Both laboratory and field studies were examined. Appropriate data from these studies were input to EMSOFT to simulate the experiments. The results of the simulations are compared with the measurements to characterize the accuracy of the EMSOFT model and its strengths and weaknesses.

5.1 MODEL SENSITIVITY TO INPUT PARAMETERS

Before performing the model validation, it was important to understand the model's sensitivity to the key input parameters. Understanding this sensitivity informs the user as to which parameters are most important to specify accurately. The sensitivity of the EMSOFT model to its key inputs is discussed below based on prior sensitivity findings by Jury et al.

Jury et al. (1983) discussed results of a sensitivity analysis of the physical-chemical properties that initialize the model upon which EMSOFT is based. The dependence of volatilization from the soil was simulated by varying evaporation, boundary layer thickness, water content, depth of incorporation, Henry's law constant (K_H), organic carbon partition coefficient (K_{oc}), and half life. Only pesticides were studied in this analysis. Two of the pesticides, lindane and dieldrin, were included in the EMSOFT model validation.

Jury et al. tested each parameter by selecting a base value and then varying it by three times its value and one-third its base value. The simulations were extended for a 20 day time period. When K_H was examined, lindane showed an order of magnitude variation in volatilization for the first day, but by day 10 had no perceivable difference. Dieldrin, on average, varied by half an order of magnitude for the tested values.

When the organic carbon partition coefficient was varied, lindane and dieldrin volatilization were consistently about an order of magnitude different for the range of values tested. Tests of half life, on the other hand, showed no difference in volatilization for either dieldrin or lindane using

three times the base case or one-third of the base case's value. (Some other chemicals did show a large difference by the end of the simulation time.)

Dieldrin showed little difference in volatilization when the soil water content, boundary layer thickness, and evaporation rate were varied. There was only a slight variation in the soil flux during the first five days of the boundary layer variation. This difference was slightly greater with lindane, up to an order of magnitude, on varying the boundary layer over the first five days. Lindane did show increasing sensitivity to evaporation variability with time.

Many of the other chemicals simulated responded differently than lindane and dieldrin. According to Jury, a chemical's soil flux dependence on boundary layer will not be significant if the vapor flux is equal to the diffusive and convective flux through the soil. Also, if the convective flux is small compared to the diffusive flux (K_H and K_{oc} are large), then evaporation rate will not be an important parameter. Jury derived a value of K_H equal to 2.65e-05 to determine a chemical's dependency on boundary layer. Chemicals with K_H values less than this value are controlled by the boundary layer thickness.

5.2 DATA SET SELECTION

A literature search was performed and researchers contacted to identify data sets for this validation. The EMSOFT model predicts emissions from soil based on knowledge of the soil and chemical properties. Soil type, chemical concentration in the soil, bulk density, water content, porosity, porewater flux, and fraction of organic carbon are important model input parameters. Therefore, the search sought to find recent and past experimental studies containing some or all of these input parameters and surface air emission flux measurements.

Numerous references were identified with potentially useful data sets as a result of this literature search. Table 5-1 lists six references which report on the four measurement studies which were selected for this model validation. The studies include both soil surface flux measurements plus adequate soil input data to test the model.

TABLE 5-1. REFERENCES WITH DATA SETS USED FOR EMSOFT VALIDATION

Environmental Quality Management, Inc. 1992.
Limited Validation of the Hwang and Falco Model for the Emissions of Soil-incorporated Volatile Organic Compounds.
Presentation of historical data in model validation study. Discusses the laboratory studies by Farmer et al. (1972 and 1974) of the volatilization of the pesticides lindane and dieldrin from soil. Also, discusses the field study by Radian Corporation of petroleum VOC emissions from soil piles.

Jury, W.A., R. Grover, W.F. Spencer and W.J. Farmer. 1980.
Modeling Vapor Losses of Soil-Incorporated Triallate.
Laboratory study of the volatilization of the pesticide triallate from soil.

Mayer, R., J. Letey, and W. J. Farmer. 1974.
Models for Predicting Volatilization of Soil-Incorporated Pesticides.
Presentation of historical data from laboratory studies compared with authors' model predictions. Includes study of lindane and dieldrin emissions from soil by Spencer and Cliath (1973).

Radian Corporation. 1989.
Short-Term Fate and Persistence of Motor Fuels in Soils.
Field study of VOC emissions from contaminated soil piles. Emission measurements were made using a surface isolation flux chamber.

Spencer, W. F., M. M. Cliath, W. A. Jury, and L. Zhang. 1988.
Volatization of Organic Chemicals from Soil as Related to Their Henry's Law Constants.
Presentation of historical laboratory studies, including the experiments of Spencer and Cliath (1973).

U.S. Environmental Protection Agency. 1991.
Database of Emission Rate Measurement Projects - Technical Note. Office of Air Quality Planning and Standards. EPA-450/1-91-003.
Compilation of data from numerous isolation flux chamber measurement studies, including the Radian field study of VOC emissions from soil piles.

As can be seen, a limited number of emission measurement studies were selected with available data suitable for this model comparison. Several other short-term studies originally identified as candidates were disqualified because the initial chemical concentrations in the soil were so high that Henry's law would not govern the liquid-air partitioning over the duration of the study. Applicability of Henry's law is an inherent assumption in the EMSOFT model. The EPA 1991 report identifies various soil flux chamber measurement studies, but does not provide enough soil setting information to perform a simulation of the quality desired for model validation.

5.3 DESCRIPTION OF SELECTED DATA SETS

Each of the data sets selected for the model validation is presented below. The original studies are briefly described and the data obtained from them identified. Chemical property data required as input to the model were often found in sources other than the measurement study reports.

Sometimes, multiple values were found in different sources for certain parameters, and these were explored in the validation simulations. The values chosen for our "base case" simulations are marked with an asterisk in the listings below. In a few cases, default values were assumed for certain inputs, following the example of Jury et al. in their simulations. The sources of all input values are identified below.

Three soil parameters were commonly calculated based on related data provided in the study reports. Soil porosity, when not given in the literature, was derived from the soil bulk density according to the following relationship:

Porosity = 1 - (bulk density / particle density).

Particle density is relatively constant among soils, varying between 2.6 and 2.8 g/cm^3. A particle density of 2.65 was assumed in all calculations of soil porosity.

Fraction of organic carbon (f_{oc}), when not specified in a study, was derived from the soil organic matter content. According to Page et al. (1982):

Organic matter content = 1.72 x organic carbon content.

This relationship was used to estimate f_{oc} whenever it was not given in a study report.

5.3.1 Farmer et al. (1972 and 1974)

These researchers performed laboratory studies of the volatilization of two pesticides, dieldrin and lindane, from soils. These data were studied in a model validation study of another soil air emissions model, the Hwang-Falco model (EQ, 1992). The input data were obtained from the EQ report.

In Farmer's experiments, the pesticides (C-14 labeled) were incorporated into Gila silt loam soil at a concentration of 5 or 10 μg/g. Water was added to the soil to bring its initial moisture content to 10 percent by weight. The soil was placed in a shallow pan, 5 mm deep, 29 mm wide and 95 mm long, which was then placed in a glass volatilization chamber. An air flow of 8 ml/s was maintained through the chamber. Relative humidity was maintained at 100 percent and temperature was a constant 30 C. The exiting air stream was passed through 25 ml of ethylene glycol to trap the dieldrin and lindane. The ethylene glycol was extracted then analyzed for the pesticides by scintillation and gas chromatography. Duplicate runs were made of all experiments.

The following experimental parameters were used as inputs for the EMSOFT simulation:

- Depth of cover: 0 cm
- Soil thickness: 0.5 cm
- Initial soil concentration: 5 or 10 μg/g
- Fraction organic carbon: 0.0058
- Soil water content: 0.075 (7.5% by volume)
- Soil bulk density: 0.75 g/cm^3
- Soil porosity: 0.72 (calculated)
- Temperature: 30 C
- Evaporation rate: 0
- Effective windspeed: 0.018 mi/h

The following chemical property values were used:

Lindane

Organic carbon partition coefficient, K_{oc}:	1080* ml/g (Lyman 1990 and EQ 1992) 1300 ml/g (Jury 1983 and 1984b)
Henry's law constant, K_H:	2.2e-05 (Lyman 1990) 3.2e-04* (EPA 1989 and EQ 1992) 1.3e-04* (Spencer 1988)
Air diffusion coefficient:	4692 cm^2/day (EQ 1992)
Water diffusion coefficient:	0.432 cm^2/day, default value (Jury 1983)
Half life:	13.8 - 240* days (Howard et al. 1991) 266 days (Jury 1984)
Boundary layer thickness:	0.12* cm (Jury 1984c) 1.2 cm (Jury 1984c)

Dieldrin

Organic carbon partition coefficient, K_{oc}:	1700* ml/g (EQ 1992) 12,000 ml/g (Jury 1984b)
Henry's law constant, K_H:	2.8e-03* (EPA 1989) 1.3e-03 (Jury 1984b) 6.7e-04 (Jury 1983) 1.8e-05 (EQ 1992) 8.9e-06 (Lyman 1990)
Air diffusion coefficient:	4216 cm^2/day (EQ 1992)
Water diffusion coefficient:	0.432 cm^2/day, default value (Jury 1983)
Half life:	175 days - 3 years* (Howard et al. 1991) 868 days (Jury 1984)
boundary layer thickness:	0.78 cm (Jury 1984c)

*Value used in base case simulation.

5.3.2 Radian Corporation (1989)

This study was a field test of soil piles contaminated with benzene, toluene, ethyl benzene and xylene (BTEX). Information was obtained both from the original reference and the EQ 1992 report, which also described an evaluation using this data set. In this experiment, management practices of VOC-contaminated soils were evaluated in terms of their relative air emissions. Comparative tests were run between soil piles subject to aeration or mixing, soil venting, heating, and no activity (control test). EMSOFT was evaluated with the control test data.

The volatilization losses of the four petroleum compounds BTEX were measured in the Radian study. The initial soil pile was prepared by mixing 132 liters of gasoline with 7900 pounds of soil. This pile was prepared and mixed as 22 smaller batches to assure uniform distribution of the BTEX. Water was added to bring the moisture content to 10 percent by weight. The soil temperature was kept between 50 and 70 F (10 - 21 C) throughout the test, and the soil pile was protected from precipitation.

BTEX air emissions and soil concentrations were measured for the control pile over 7 weeks. Air emissions were measured with an isolation flux chamber. The flux chamber is a dome-shaped apparatus placed on top of a known surface area of exposed soil, typically one square meter. A known flow rate of sweep air is drawn through the chamber above the soil surface (similar to the lab experiments evaluated here). This air was analyzed to measure BTEX flux. Grab samples were collected in 100-ml gas-tight syringes which were then analyzed for BTEX by gas chromatography. These data were used to calculate the instantaneous flux of each compound at the time the sample was taken.

The following experimental parameters were used as inputs for the EMSOFT simulation:

- Depth of cover: 0 cm
- Soil thickness: 91 cm
- Initial soil concentration: benzene: 110 μg/g
  toluene: 880 μg/g
  ethyl benzene: 310 μg/g
- Fraction organic carbon: 0.02
- Soil water content: 0.15 (15% by volume)
- Soil bulk density: 1.5 g/cm^3
- Soil porosity: 0.43 (calculated)
- Temperature: 20 C

No information was provided in the source documents regarding evaporation rate, windspeed or boundary layer thickness. For the model simulation, zero evaporation and a typical windspeed of 3 m/s (6.7 mi/h) were assumed. A boundary layer thickness of 0.5 cm was calculated using Equations 27 and 28 given in Section 3.4.5, based on this windspeed.

The following chemical property values were used:

Benzene

Organic carbon partition coefficient, K_{oc}:	83 ml/g (EQ 1992)
Henry's law constant, K_H:	0.23 (EQ 1992) verified with EPA 1989
Air diffusion coefficient:	7603 cm^2/day (EPA 1989)
Water diffusion coefficient:	0.847 cm^2/day (EPA 1989)
Half life:	5 - 16* days (Howard et al. 1991)

Toluene

Organic carbon partition coefficient, K_{oc}:	300 ml/g (EQ 1992)
Henry's law constant, K_H:	0.26 (EQ 1992) verified with EPA 1989
Air diffusion coefficient:	7517 cm^2/day (EPA 1989)
Water diffusion coefficient:	0.743 cm^2/day (EPA 1989)
Half life:	4 - 22* days (Howard et al. 1991)

Ethyl Benzene

Organic carbon partition coefficient, K_{oc}:	1100 ml/g (EQ 1992)
Henry's law constant, K_H:	0.27 (EQ 1992) verified with EPA 1989
Air diffusion coefficient:	6480 cm^2/day (EPA 1989)
Water diffusion coefficient:	0.674 cm^2/day (EPA 1989)
Half life:	3 - 10* days (Howard et al. 1991)

*Value used in base case simulation.

5.3.3 Jury et al. (1980)

Jury et al. (1980) conducted laboratory experiments to measure the vapor loss of triallate [S-(2,3,3-trichloroallyl) diisopropyl-thiocarbamate] from two different soils with and without water evaporation. One of these experiments was used in the model validation.

Triallate was incorporated into a San Joaquin sandy loam soil at a concentration of 10 µg triallate per gram of soil. A soil column 10 cm deep and 30 cm^2 was placed in a volatilization chamber. An air flow rate of 1 liter per minute was maintained through the chamber, yielding an effective windspeed across the soil surface of 1 km/h. The soil column was wetted from the bottom through porous ceramic tubes in the chamber base plate. In the test evaluated here, 100 percent relative humidity was maintained in the air above the soil. Temperature was held at 25 C. The exit air stream was passed through polyurethane foam (PUF) plugs to trap the triallate as daily samples.

The experiment was carried out for thirty days. The PUF plugs were analyzed according to a cross-referenced method (Grover et al., 1978).

The following experimental parameters were used as inputs for the EMSOFT simulation:

- Depth of cover: 0 cm
- Soil thickness: 10 cm
- Initial soil concentration: 10 μg/g
- Fraction organic carbon: 0.0072 (calculated)
- Soil water content: 0.28 (28% by volume)
- Soil bulk density: 1.34 g/cm^3
- Soil porosity: 0.5
- Temperature: 25 C
- Evaporation rate: 0
- Effective windspeed: 0.28 m/s

The following chemical property values were used:

Triallate

Organic carbon partition coefficient, K_{oc}:	3600 ml/g (Jury 1990)
Henry's law constant, K_H:	7.9e-04 (Jury 1990)
Air diffusion coefficient:	3888 cm^2/day (Jury 1980)
Water diffusion coefficient:	0.432 cm^2/day, default value (Jury 1983)
Half life:	100 days (Jury 1980)
Boundary layer thickness:	0.4 cm (Jury 1984c)

5.3.4 Spencer and Cliath (1973)

Spencer and Cliath measured the volatilization of two pesticides, lindane and dieldrin, from a Gila silt loam soil in the laboratory. Information on this study was obtained from two secondary sources: Jury et al. (1984) and Mayer et al. (1974).

A 25-day chamber test was performed. The initial soil concentrations of lindane and dieldrin were 10 μg/g. The soil column depth was 11 cm. The soil moisture content was kept at

23 or 27 percent by weight (lindane and dieldrin tests, respectively) and temperature kept at 30 C throughout the test. The air flow through the chamber was 2.15 cm/s.

The following experimental parameters were used as inputs for the EMSOFT simulation:

- Depth of cover: 0 cm
- Soil thickness: 11 cm
- Initial soil concentration: 10 μg/g
- Fraction organic carbon: 0.0035 (calculated)
- Soil water content: 0.27 (27% by volume) for dieldrin
  0.23 (23% by volume for lindane
- Soil bulk density: 1.4 g/cm^3
- Soil porosity: 0.47 (calculated)
- Temperature: 30 C
- Evaporation rate: 0
- Effective windspeed: 2.15 cm/s

The same chemical properties used for lindane and dieldrin in the Farmer et al. simulation were used for this study.

5.4 MODEL VALIDATION RESULTS

The data sets discussed in Section 5.3 were modeled with EMSOFT to compare predicted emission fluxes to measured values. In order to run these simulations, the model inputs had to be determined from the available references. For these case studies, most of the model inputs were available. Those that were not explicitly stated in the source documents were either documented in other references, calculated based on known chemical or soil properties, or assumed to be similar to those cited in other studies.

The EMSOFT model was used with the data sets presented in Section 5.3 for the model validation. Then, for some data sets, the model's sensitivity to parameter variability was tested by remodeling a data set with one input, such as the Henry's law constant, set equal to a new value. This was necessary because in searching for data for this modeling exercise, different values for

some "constants" were cited. Also, if an uncertainty existed in an input value selected, such as the surface boundary layer, an alternative value was tested.

To interpret the EMSOFT results, the amount of underprediction or overprediction of modeling results was determined. For example, a 30 percent underprediction means that 70 percent of the measured flux was predicted.

Farmer et al. (1972 and 1974)

As discussed in Section 5.3, lindane and dieldrin emission fluxes were measured from soil with initial concentrations of 5 or 10 µg/g. Lindane simulations are presented first, followed by dieldrin.

Lindane

Figure 5-1a presents the EMSOFT modeling results using the data set described above for a soil concentration of lindane at 10 µg/g (base case). After one day, the predicted emission flux of 0.00065 mg/cm^2/day was less than the measured emission flux of 0.00116 mg/cm^2/day. While the overall trend of the model predictions followed measured values, the model continued to underpredict by about 50 percent through the experiment's completion on day 7.

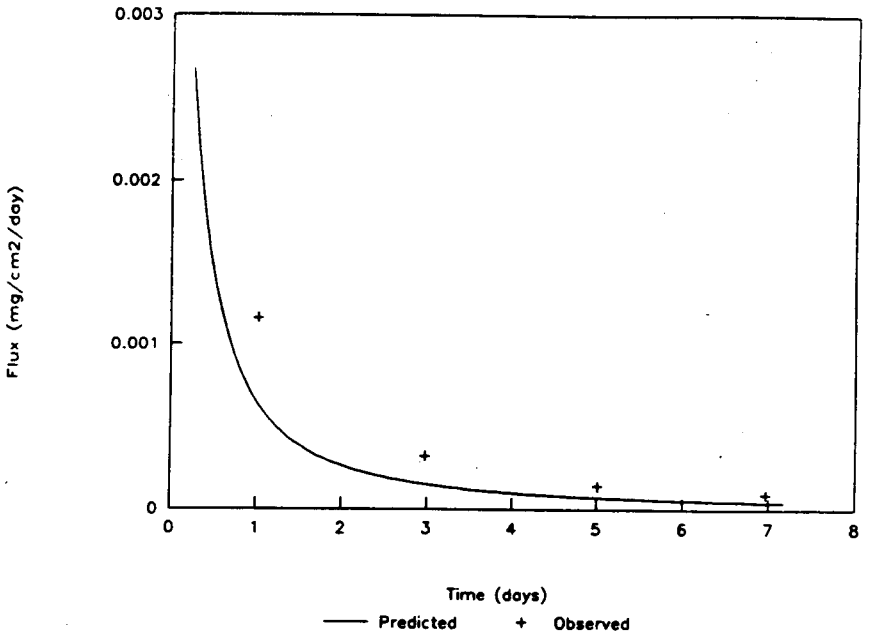

Figure 5-1a. Predicted and observed lindane flux, Farmer 10 mg/kg - base case.

For lindane, conflicting values for some of the input variables were cited by different sources. It was beyond the scope of this validation to determine the validity of these values. However, because an EMSOFT user may find more than one choice for a variable, a sensitivity analysis was included in this model validation exercise. The alternative variables for the lindane validation included an organic carbon partition coefficient of 1300 ml/g (Jury 1983 and 1984b), dimensionless Henry's constant of 2.2e-05 at 20 C (Lyman 1990) and a lower half life of 14 days (Howard et al., 1991).

The EMSOFT model was evaluated for these alternative cases. Using the alternative K_{oc} value of 1300 ml/g resulted in a negligible change (Figure 5-1b) from the base case. Applying a smaller Henry's constant of 2.2e-05, the model initially underpredicted more than the base case. However, by day 5, predicted EMSOFT emissions approximately equaled observed values. These results can be seen in Figure 5-1c. Using a half life of 14 days instead of 240 days resulted in model underestimates of observed emissions by an additional 10 percent lower than the original case on an average, and about 25 percent lower by day 7 (Figure 5-1d).

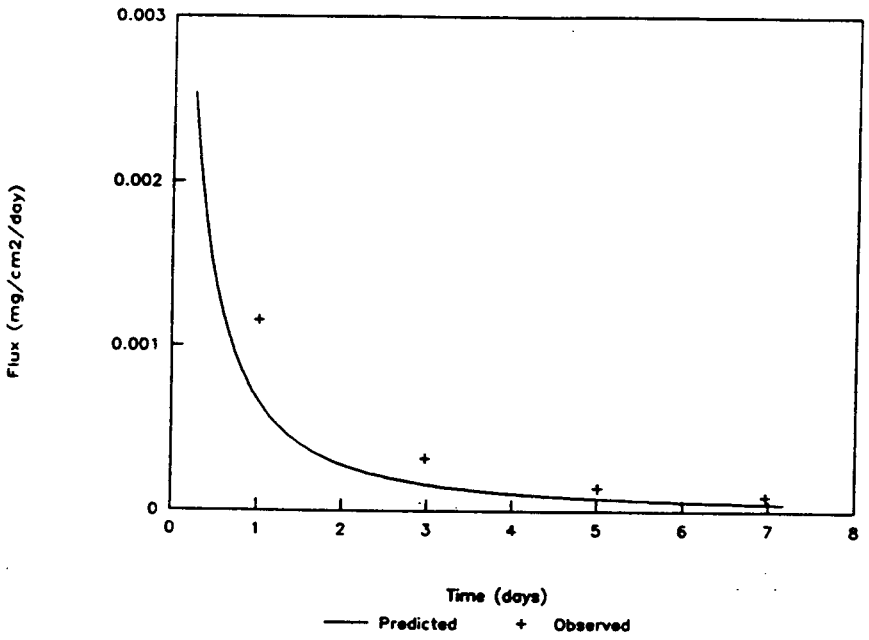

Figure 5-1b. Predicted and observed lindane flux, Farmer 10 mg/kg - K_{oc} = 1300 ml/g.

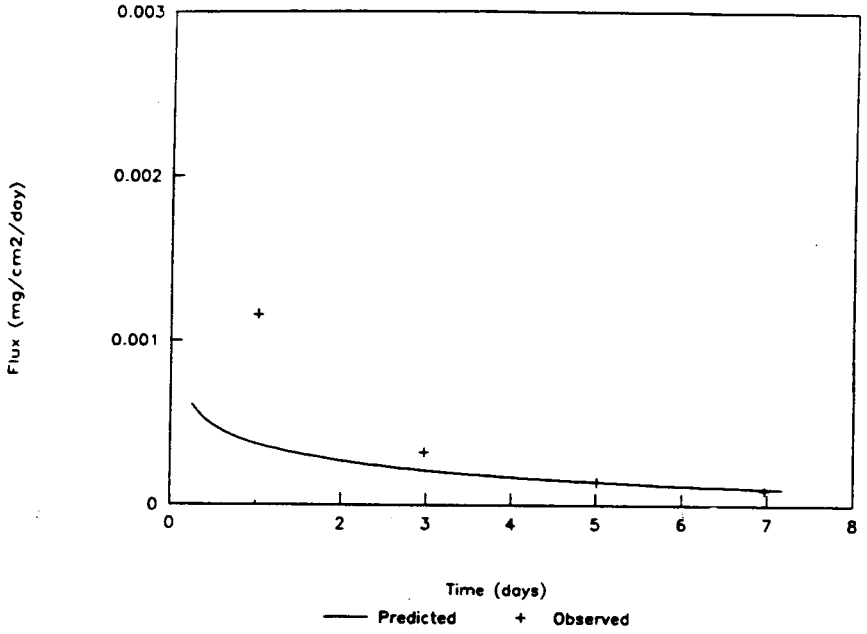

Figure 5-1c. Predicted and observed lindane flux, Farmer 10 mg/kg - K_H = 2.23-05.

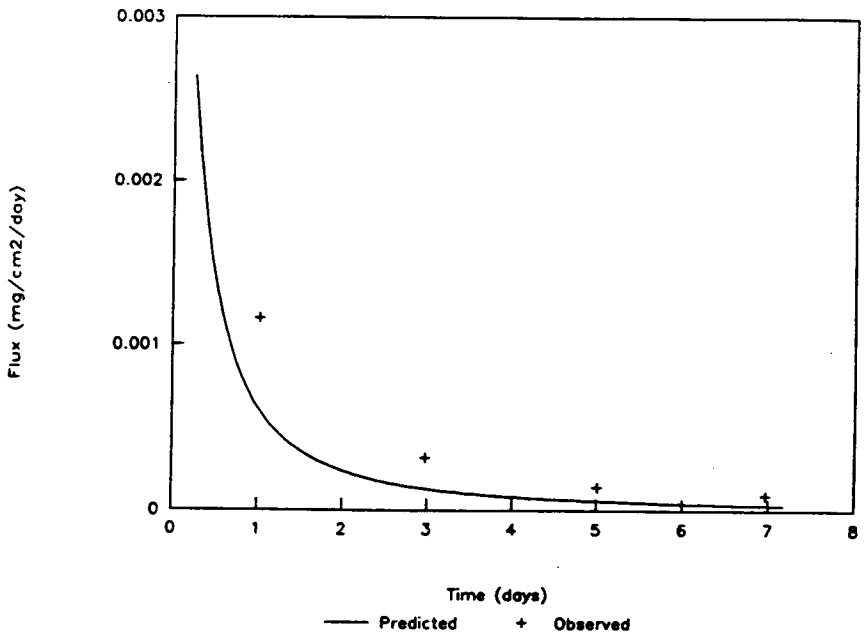

Figure 5-1d. Predicted and observed lindane flux, Farmer 10 mg/kg - half life = 14 days.

EMSOFT predicted emissions and observed values for the 5 µg/g lindane case are shown in Figure 5-2. For day 1, the predicted emission flux underestimated the observed flux of 0.0005 mg/cm^2/day by about 30 percent. Predictions decreased faster than observed emission fluxes during the first few days, then decreased proportionally to observed values over longer time periods.

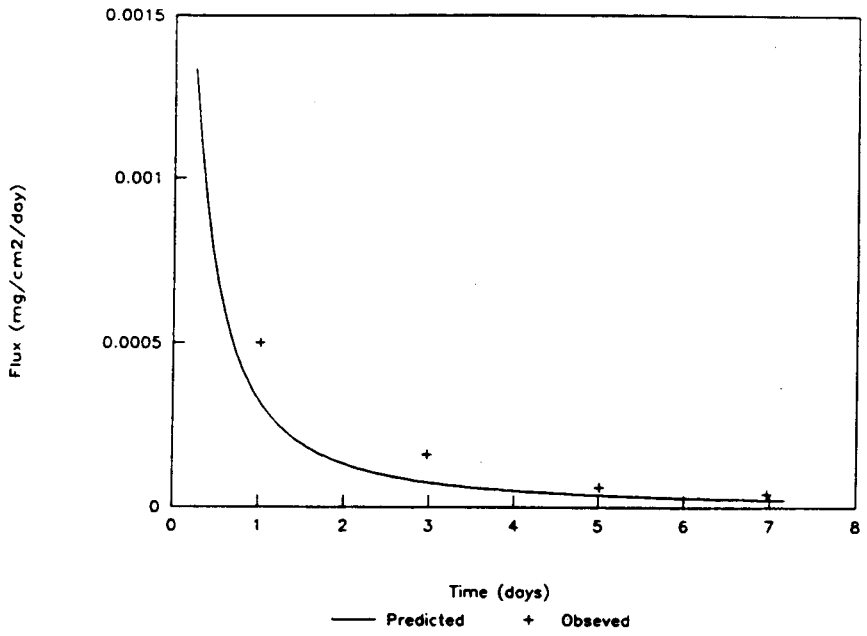

Figure 5-2. Predicted and observed lindane flux, Farmer 5 mg/kg.

Dieldrin

The other Farmer et al. experiment measured dieldrin emission fluxes from soil with initial dieldrin concentrations of 10 µg/g and 5 µg/g. Using the data set given in Section 5.3 for the 10 µg/g soil concentration, the EMSOFT model predicted dieldrin emissions as shown in Figure 5-3a. The model overpredicted emissions by 50 percent for the first day and then underpredicted emissions 50 to 80 percent for days 5 through day 12.

The results shifted when an alternative K_{oc} value of 12,000 ml/g was used (Jury 1984b), as shown in Figure 5-3b. The predicted emissions decreased with time more gradually than with the base case value of 1700 ml/g. EMSOFT overpredicted observations initially by 64 percent, nearly matched the observed values for days 4 through 7, and underpredicted emissions by 52 percent by day 12.

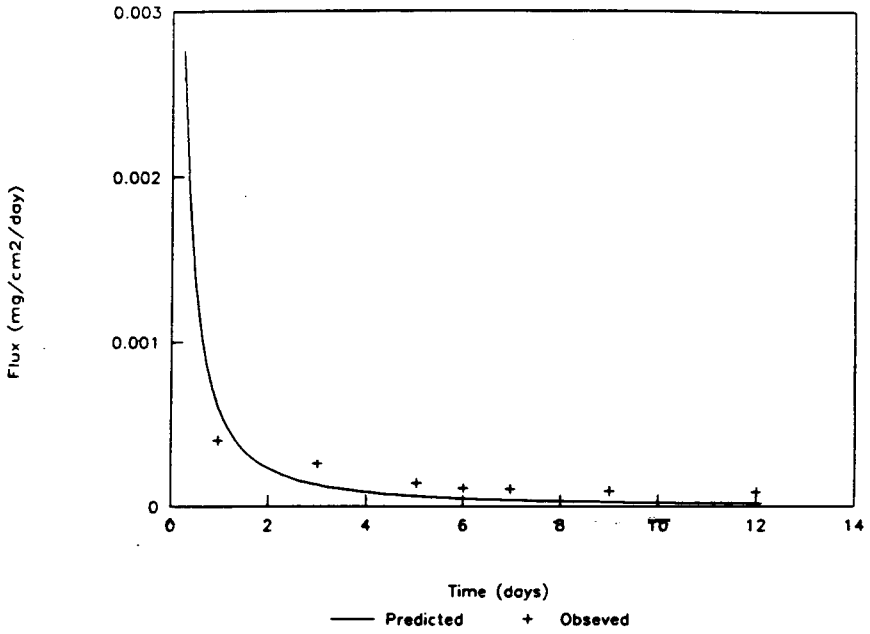

Figure 5-3a. Predicted and observed dieldrin flux, Farmer 10 mg/kg - base case.

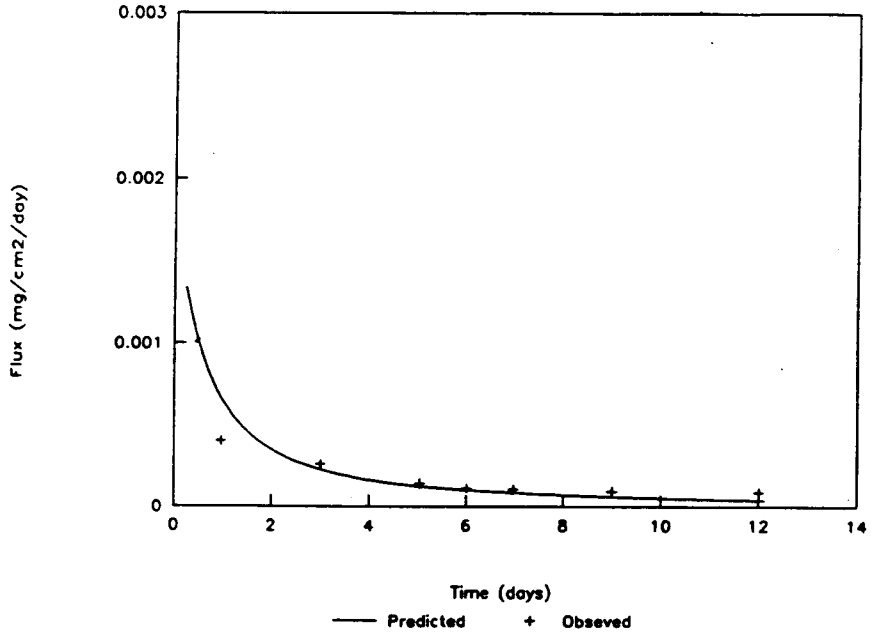

Figure 5-3b. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_{oc} = 12,000 ml/g.

Two alternative Henry's law constants were used, 6.7e-04 (Jury 1983) and 8.9e-06 (Lyman 1990); see Figures 5-3c and 5-3d, respectively. Lowering the Henry's law constant decreased predictions dramatically.

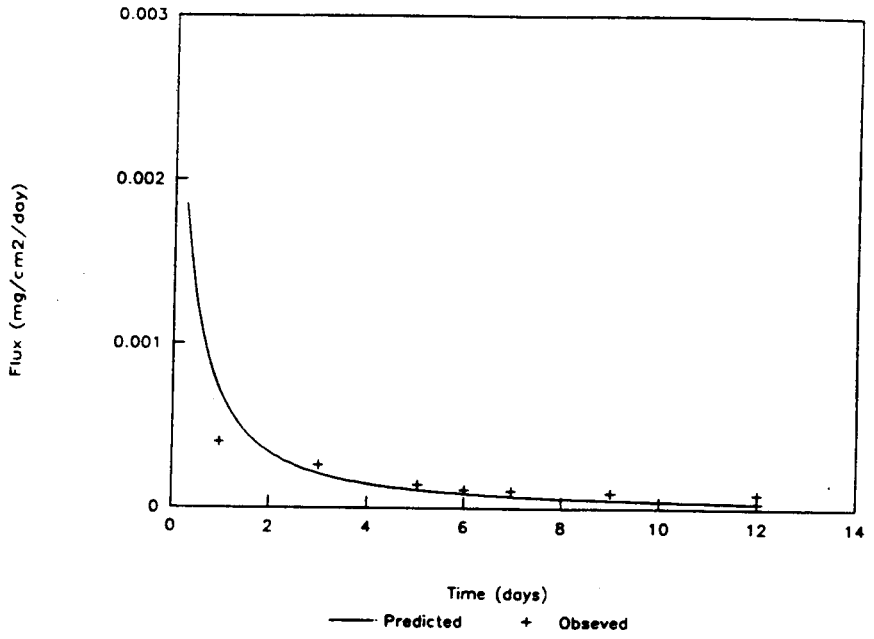

Figure 5-3c. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_H = 6.7e-04.

Figure 5-4 presents the results of the EMSOFT modeling analysis using the 5 µg/g lindane soil concentration. These results show a trend similar to the 10 µg/g case. Emissions were overpredicted for day 1 by 45 percent but underpredicted by 43 percent on day 3. The underestimation increased with time, showing underprediction of 68 percent by day 7 and 78 percent by day 12.

Ethyl benzene emissions were predicted by the EMSOFT model using the data set described in Section 5.3. The results for this analysis are presented in Figure 5-5. The emission fluxes agreed well with observations for the first 5 days. The only other measurements were on day 21 and day 29. EMSOFT underpredicted ethyl benzene emissions by 24 and 48 percent, respectively.

Benzene emission fluxes from soil were also measured in the Radian study. Benzene was selected for sensitivity tests as part of this model validation since it is a frequently studied VOC.

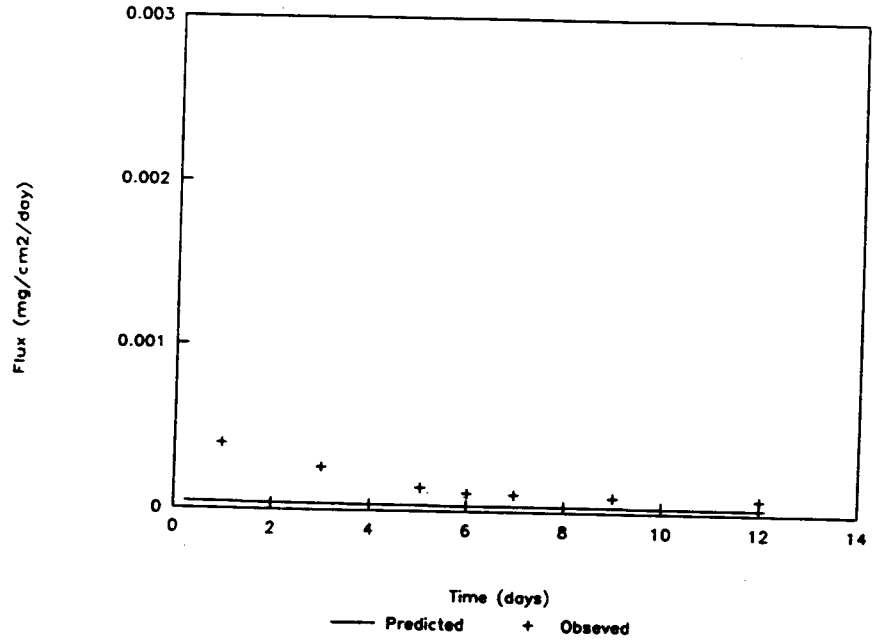

Figure 5-3d. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_H = 8.9e-06.

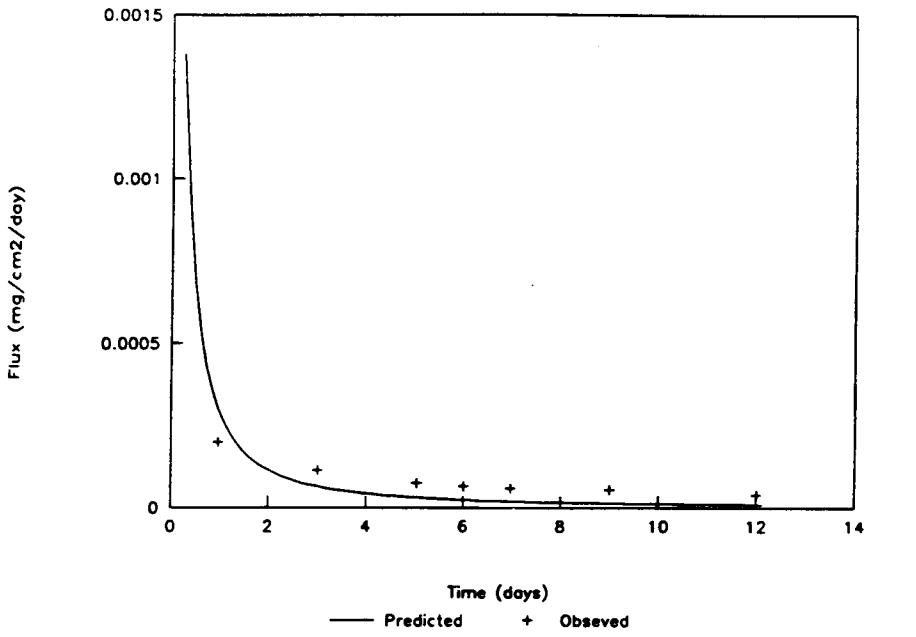

Figure 5-4. Predicted and observed dieldrin flux, Farmer 5 mg/kg.

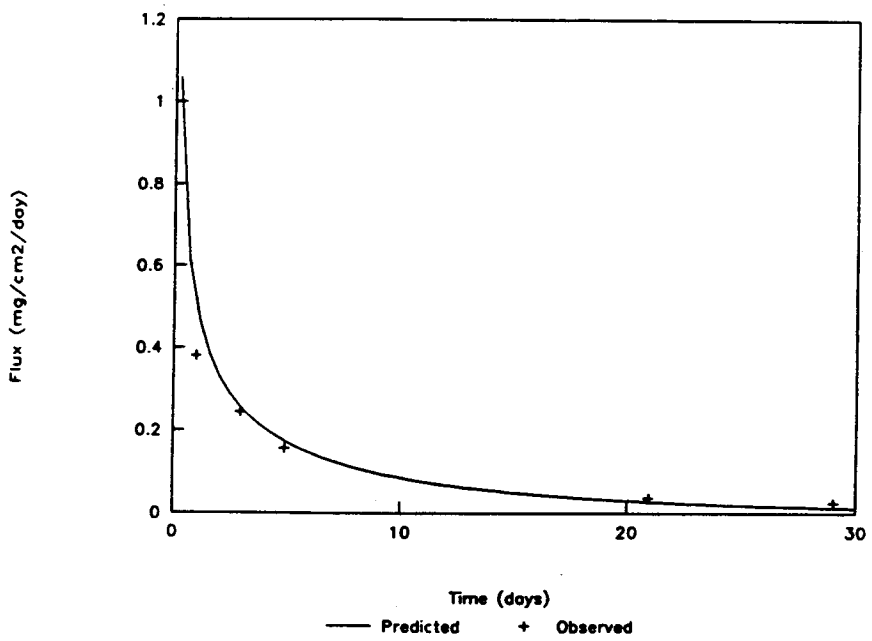

Figure 5-5. Predicted and observed ethyl benzene flux, Radian 310 mg/kg.

The air and water diffusion coefficients, the depth of the surface boundary layer, and the chemical half life were varied.

Using the benzene data set from Section 5.3, benzene emissions were overpredicted by a factor of 2 for the first third of the experiment (see Figure 5-6a). Once again, measured flux values were only available for the beginning and end of the experimental period. The model under-predicted emission fluxes by 13 percent at day 21 and by 37 percent at day 29.

The EMSOFT User's Guide lists default air and water diffusion coefficients (Jury et al. 1983) of 4320 cm^2/day and 0.432 cm^2/day based on Jury's prior research (Jury et al., 1983). Unlike the pesticides modeled in the Farmer study, benzene's diffusion coefficients are about 50 percent greater than these default values (EPA, 1989). When the default values were chosen (a possibility if the correct reference is not readily available), the predicted benzene emissions (see Figure 5-6b) showed better agreement within the first 5 days than predictions made with the actual diffusion coefficients for this time. However, at day 21, the predicted emissions with the default coefficients underpredicted the measured emissions to a greater extent than those predicted with the actual coefficients. This trend continued to day 29.

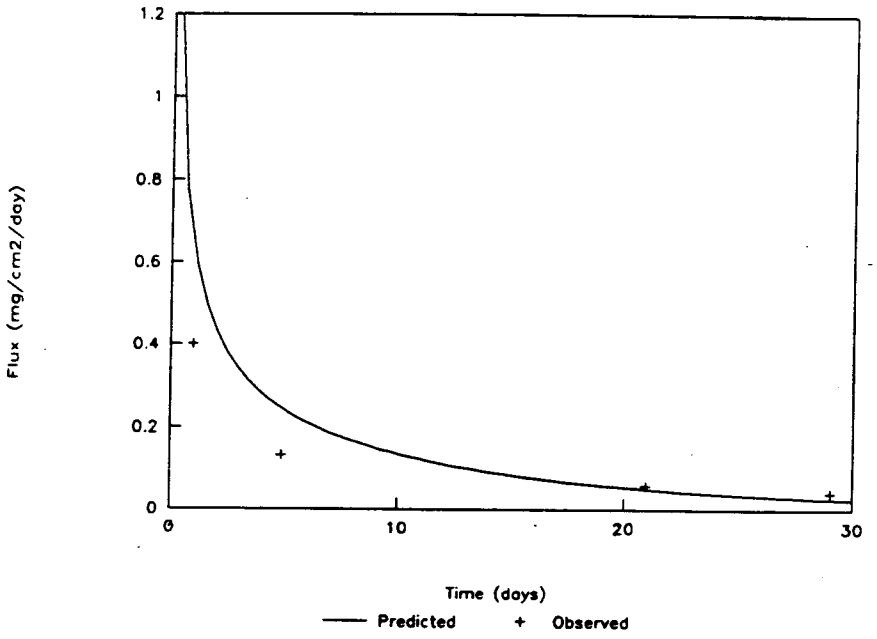

Figure 5-6a. Predicted and observed benzene flux, Radian 110 mg/kg - base case.

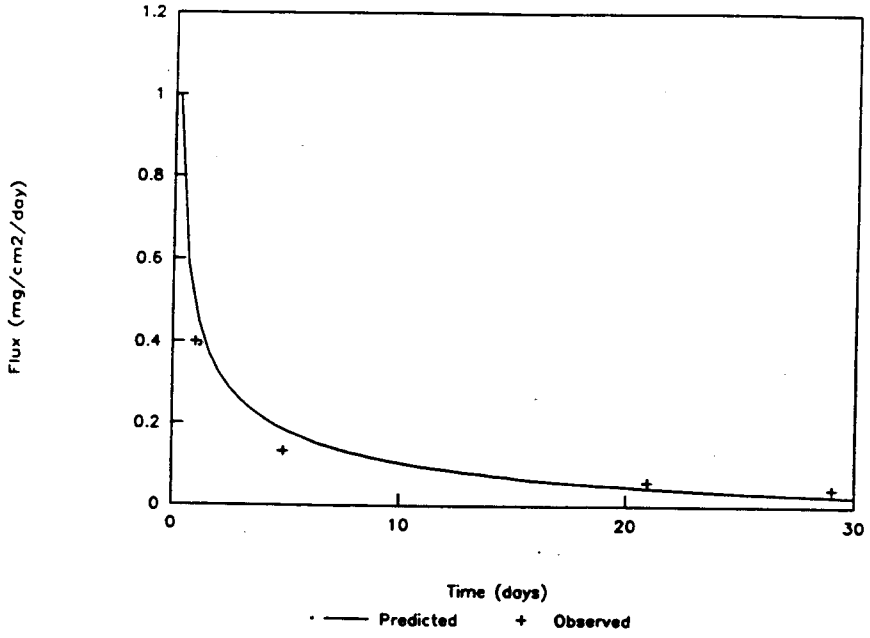

Figure 5-6b. Predicted and observed benzene flux, Radian 110 mg/kg - default diffusion coefficients.

Next, the depth of the surface boundary layer was increased from 0.5 to 1.5 cm. This did not change predictions from the original case. This result agrees with the findings of Jury et al. 1983, that high Henry's law constant compounds (K_H>2.65x10^{-5}) are not sensitive to boundary layer thickness (Figure 5-6c).

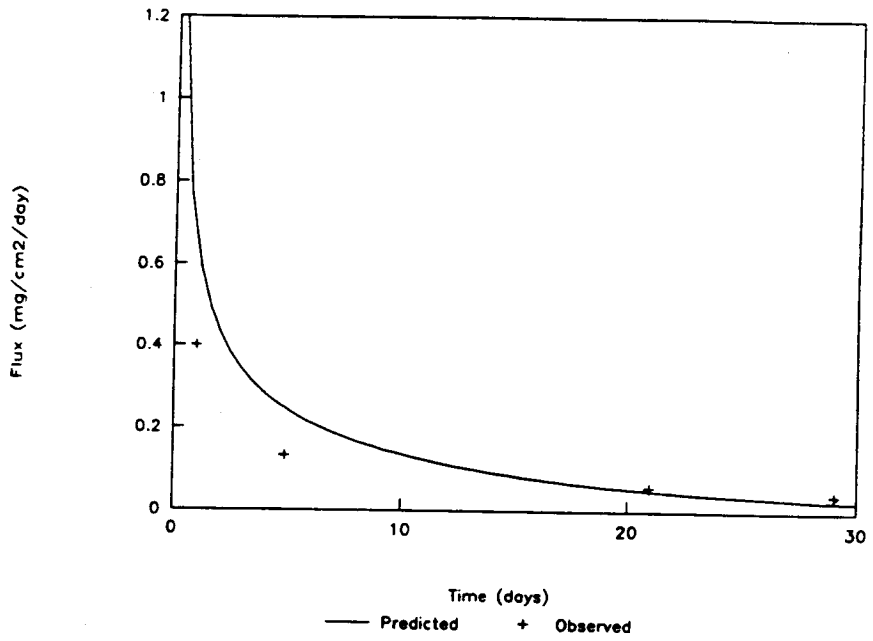

Figure 5-6c. Predicted and observed benzene flux, Radian 110 mg/kg - boundary layer = 1.5 cm.

Some references from the early 1980's used a value of 365 days to infinity for the half life of benzene. The most recent benzene half life data available (Howard et al., 1991) is based on aqueous biodegradation, not biodegradation in soil. Thus, some investigators believe that further research is needed to properly determine the half life of benzene in soil (Jury 1990a). To test the sensitivity of this parameter, EMSOFT was modeled using a benzene half life of 365 days. The results are given in Figure 5-6d. The model overpredicted for all observations, with the average of the predicted to observed emissions equal to 1.7.

Toluene emissions were predicted with EMSOFT for the data set described in Section 5.3. Shown in Figure 5-7, EMSOFT overpredict measured fluxes by an average factor of two. The measurement on day 3, which exceeds the model prediction, was deemed an outlier by Radian in their discussion of the data (Radian, 1991).

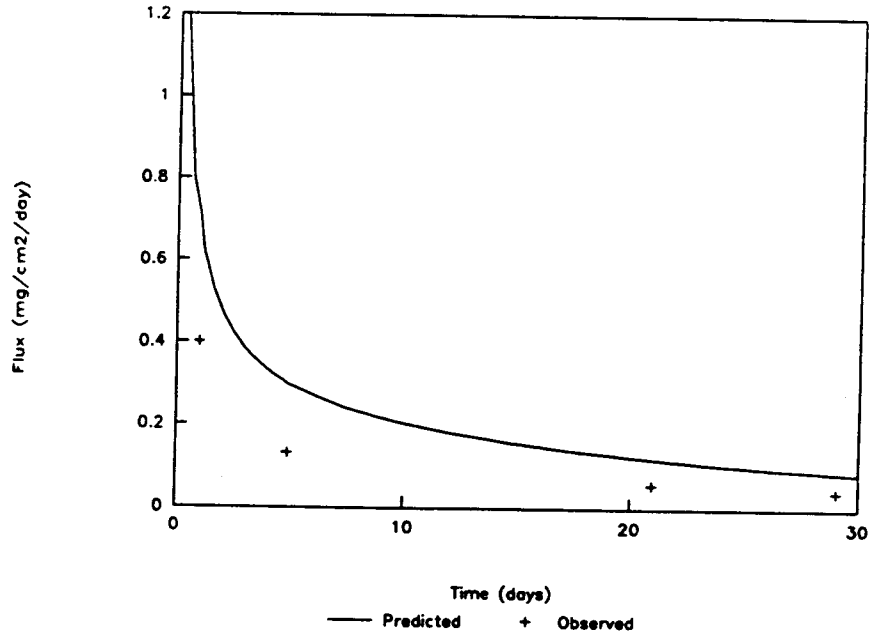

Figure 5-6d. Predicted and observed benzene flux, Radian 110 mg/kg - half life = 365 days.

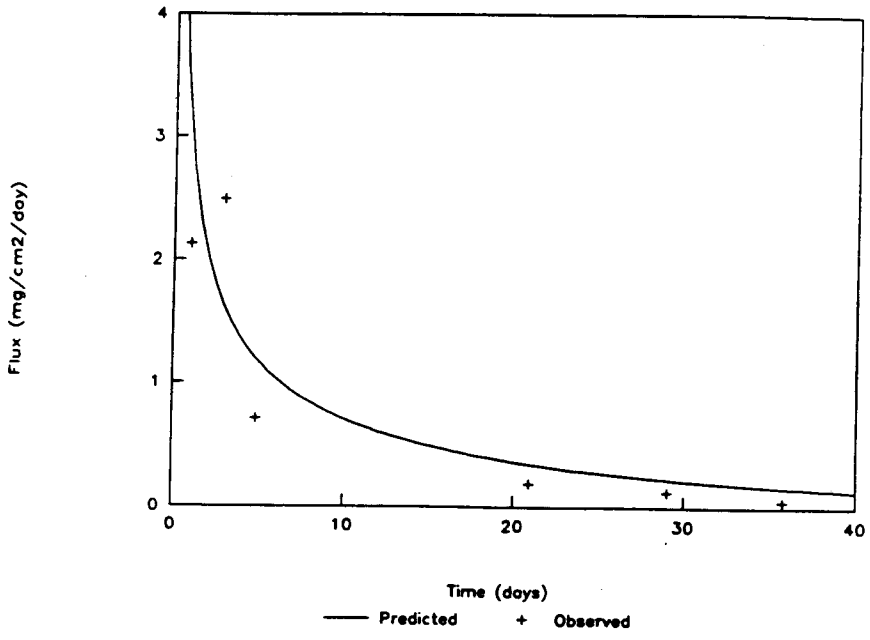

Figure 5-7. Predicted and observed toluene flux, Radian 880 mg/kg.

Jury 1980

Jury conducted an emissions flux experiment whereby triallate emissions were measured from soil containing 10 µg/g triallate. Using the variables given in Section 5.3, the EMSOFT model predicted emission fluxes as shown in Figure 5-8. The EMSOFT model predicted triallate emissions correlated very well to observed values.

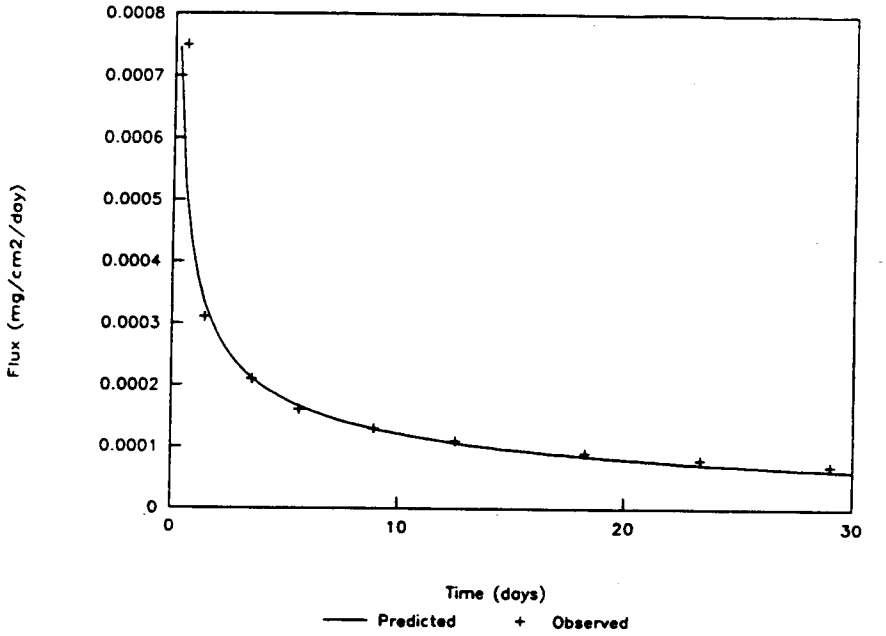

Figure 5-8. Predicted and observed triallate flux, Jury 10 mg/kg.

Spencer & Cliath 1973

Spencer & Cliath measured dieldrin and lindane fluxes from soil with a pesticide concentration of 10 µg/g. The predicted dieldrin emission fluxes are presented in Figures 5-9a and 5-9b, for surface boundary layers of 1.2 cm and 0.12 cm, respectively. No difference was attributable to the variation in surface boundary layer. The predicted dieldrin flux overestimated the observed data by approximately a factor of 4 on an average. This factor decreased somewhat by the day of the last observation.

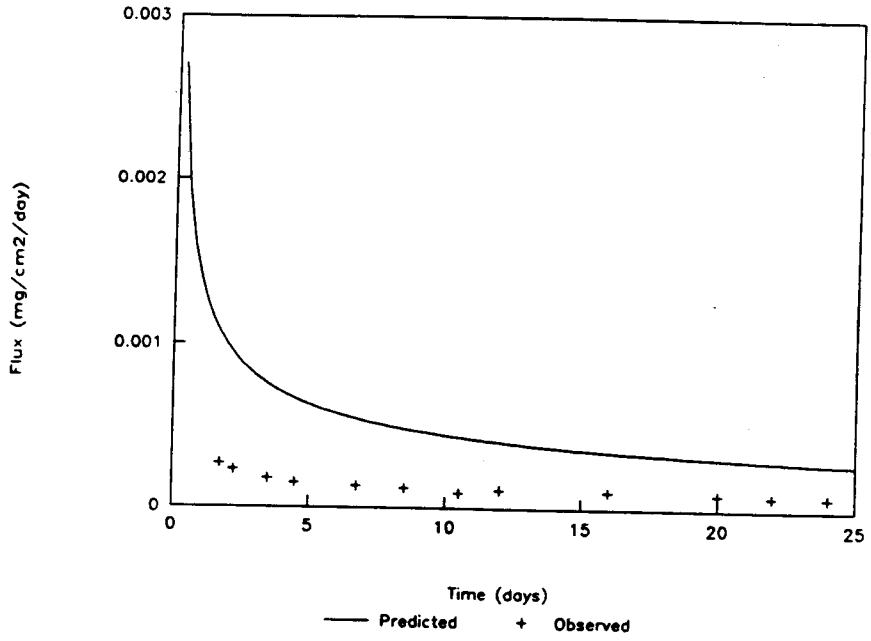

Figure 5-9a. Predicted and observed dieldrin flux, Spencer & Cliath 10 mg/kg - boundary layer = 1.2 cm.

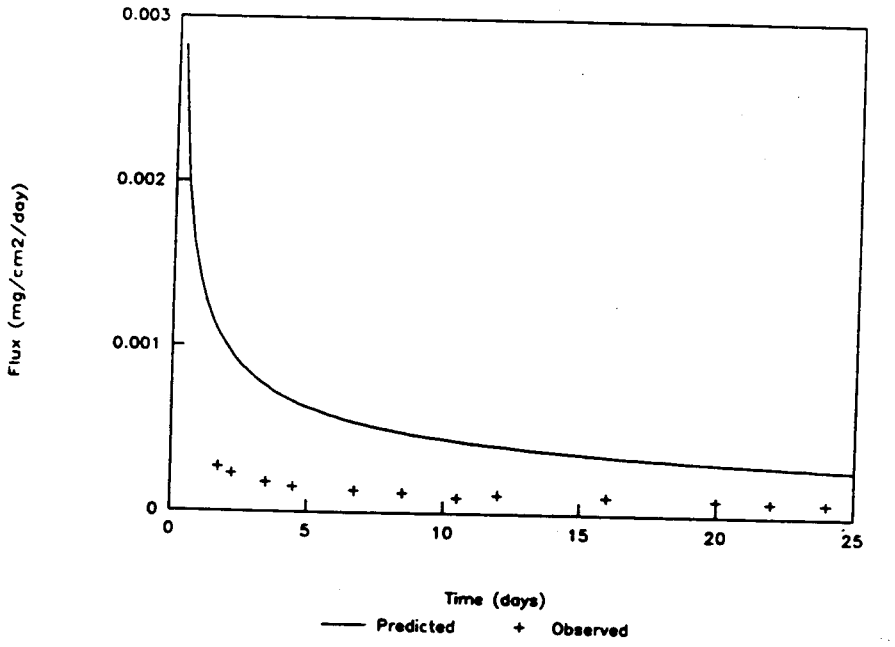

Figure 5-9b. Predicted and observed dieldrin flux, Spencer & Cliath 10 mg/kg - boundary layer = 0.12 cm.

In contrast to the dieldrin results, the EMSOFT model underpredicted lindane emission fluxes by about 50 percent as shown in Figure 5-10.

The model validation results can be summarized by calculating the ratio of the predicted flux to the measured flux for each observation in each experiment. These ratios can be summed together and averaged to get an overall indication of how the EMSOFT model did in predicting an experiment's observations. This analysis was completed for the information discussed above and is presented in Table 5-2. Average predicted-to-observed ratios are listed for the base case simulated and the alternative conditions modeled.

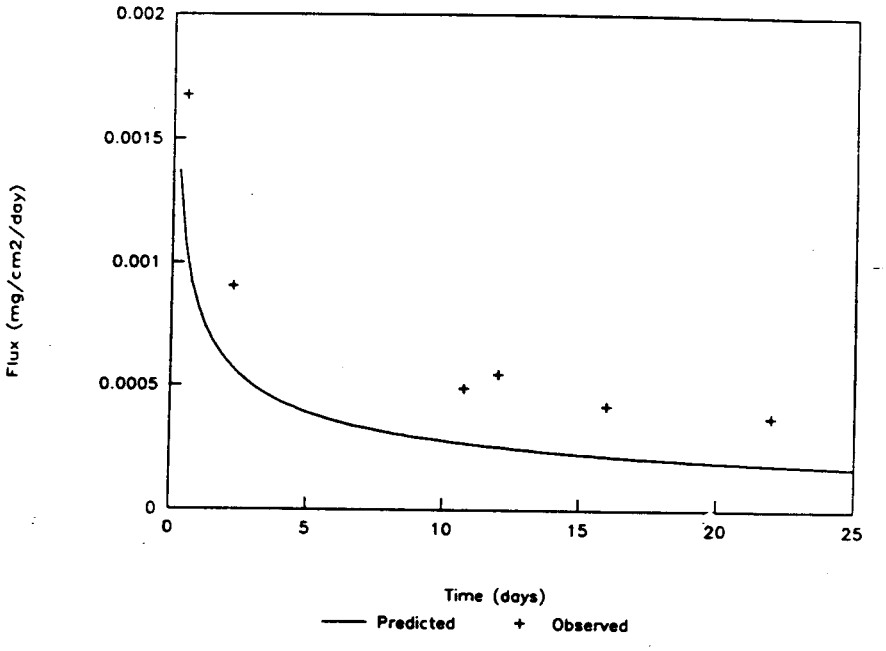

Figure 5-10. Predicted and observed lindane flux, Spencer & Cliath 10 mg/kg.

5.5 CONCLUSIONS

The performance of the EMSOFT model has been compared to the results of various measurement studies in the section above. The model performance varied with each measurement data set by overpredicting or underpredicting the observed results from those of the associated studies. Overall, the EMSOFT model provided reasonably accurate predictions for the test cases given the uncertainty of many of the input parameters.

TABLE 5-2. AVERAGE PREDICTED-TO-OBSERVED RATIOS FOR MODEL VALIDATION TESTS

Study	Chemical	Variation	Ratio of predicated flux to observed value
Farmer	Lindane (10 µg/g)	Base Case K_{oc} = 1300 ml/g $K_H = 2.2 \times 10^{-5}$ $t_{1/2}$ = 14	0.50 0.54 0.77 0.42
Farmer	Lindane (5 µg/g)	Base Case	0.56
Farmer	Dieldrin (10 µg/g)	Base Case K_{oc} = 12,000 mg/l $K_H = 6.7 \times 10^{-4}$ $K_H = 8.9 \times 10^{-6}$ $t_{1/2}$ = 175	0.53 0.88 0.81 0.26 0.52
Farmer	Dieldrin (5 µg/g)	Base Case	0.51
Radian	Ethylbenzene (310 µg/g)	Base Case	0.96
Radian	Benzene (110 µg/g)	Base Case default diffusion coef. boundary layer = 1.5 cm $t_{1/2}$ = 365	1.06 0.83 1.06 1.73
Radian	Toluene (880 µg/g)	Base Case	2.23
Spencer & Cliath	Dieldrin	Base Case boundary layer = 0.12	3.94 3.95
Spencer & Cliath	Lindane	Base Case	0.55
Jury	Triallate	Base Case	0.95

In general, the model predictions agreed with the measured fluxes within a factor of 2. In its best performances, EMSOFT nearly matched the measurement results at each time interval (Jury 1980, triallate; and Radian 1989, ethyl benzene). The poorest agreement for all data sets, including all variations of input parameters studied, was plus or minus a factor of 4.

A variety of soils and chemicals were considered in this analysis. The range of values for many of the model input parameters included in this analysis are summarized below:

- Soil thickness: 0.5 - 91 cm
- Fraction organic carbon: 0.0035 - 0.02
- Soil volumetric water content: 0.075 - 0.28
- Soil bulk density: 0.75 - 1.5 g/cm^3
- Initial chemical soil concentration: 5 - 880 µg/g
- Organic carbon partition coefficient: 83 - 12,000 ml/g
- Henry's law constant (dimensionless): 8.9e-06 - 0.27
- Half life: 10 days - 3 years
- Boundary layer thickness: 0.4 - 1.5 cm.

Clearly, this validation is limited by the range of conditions simulated. Important limitations include:

1. The duration of experiments simulated ranged from 7 to 36 days. Model performance for longer durations could not be validated.

2. The influence of porewater flux (evaporation and leaching) was not examined. This parameter is difficult to specify accurately and varies over time. Jury et al. (1983) showed that emissions of some compounds are sensitive to changes in evaporation rate.

3. Only "no cover" scenarios were simulated in this validation. Measurement studies of "clean cover" scenarios (contaminated soil covered by a layer of clean soil) were not found.

As demonstrated in some of the simulations, it is important to carefully specify the input parameters, especially those which the model may be most sensitive to, such as K_{oc}, f_{oc}, and K_H. Parameter sensitivity of the model is chemical- and setting-specific, and may be difficult to forecast. Therefore, performance of sensitivity analysis for parameters with uncertain values is highly recommended.

SECTION 6

REFERENCES

Aller, L., T. Bennett, J. H. Lehr, R. J. Petty, and G. Hackett. 1987. DRASTIC: A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings. Prepared for the U.S. Environmental Protection Agency, Office of Research and Development, Ada, Oklahoma. National Water Well Association, Dublin, Ohio. EPA-600/2-87-035.

Bonazountas, M. and J. M. Wagner. 1984. "SESOIL", A Seasonal Soil Compartment Model prepared by Arthur D. Little for U.S. EPA, Office of Toxic Substances.

Clapp, P. B. and G. Homberger. 1978. Empirical Equations for Some Soil Hydraulic Properties. Water Resources Research, Vol. 14, No. 4., pp. 601-604.

Eagleson, P. S. 1978. Climate, Soil, and Vegetation 3. A Simplified Model of Soil Moisture Movement in the Liquid Phase. Water Resources Research, Vol. 14, No. 5, pp. 722-730.

Freeze, R. A. and J. A. Cherry. 1979. Groundwater. Prentice-Hall: Englewood Cliffs, NJ. 604 pp.

Dunn, I. S., L. R. Anderson, and F. W. Keifer. 1980. Fundamentals of Geotechnical Analysis. John Wiley & Sons: New York, NY. 414 pp.

Hasset, J. J., W. L. Banwart, and R. A. Griffin. 1983. Correlation of Compound Properties with Sorption Characteristics of Nonpolar Compounds by Soils and Sediments: Concepts and Limitations in C. W. Francis and S. I. Auerback, eds., Environment and Solid Wastes: Characterization, Treatment, and Disposal. Butterworth Publishers: London. pp 161-178.

Howard, P. H., R. S. Boethling, W. F. Jarvis, W. M. Meylan, and E. M. Michalenko, 1991. Handbook of Environmental Degradation Rates. Lewis Publishers, Chelsea, Michigan. 725 pp.
Jury, W. A. undated. A Users Manual for the Environmental Fate Screening Model Programs BAM and BCM. submitted to California Department of Health Services.

Jury, W. A., R. Grover, W. F. Spencer and W. J. Farmer. 1980. Modeling Vapor Losses of Soil - Incorporated Triallate. Soil Sci. Soc. Am. J., Vol 44, pp 445-450.

Jury, W. A., W. F. Spencer, and W. J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: I. Model Description. J. Environ. Qual., Vol. 12, no. 4, pp. 558-564.

Jury, W. A., W. J. Farmer, and W. F. Spencer. 1984a. Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity. J. Environ. Qual., Vol. 13, no. 4, pp. 567-572.

Jury, W. A., W. F. Spencer, and W. J. Farmer. 1984b. Behavior Assessment Model for Trace Organics in Soil: III. Application of Screening Model. J. Environ. Qual., Vol. 13, no. 4, pp. 573-579.

Jury, W. A., W. F. Spencer, and W. J. Farmer. 1984c. Behavior Assessment Model for Trace Organics in Soil: IV. Review of Experimental Evidence. J. Environ. Qual., Vol. 13, no. 4, pp. 580-586.

Jury, W. A., D. Russo, G. Streile, and H. El Abd. 1990. Evaluation of Volatilization by Organic Chemicals Residing Below the Soil Surface. Water Resources Res. Vol 26, No. 1, pp 13-20.

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1990. Handbook of Chemical Property Estimation Methods. McGraw Hill: New York, NY.

Mayer, R., J. Letey, and W. J. Farmer. 1974. Models for Predicting Volatilization of Soil Incorporated Pesticides. Soil Sci. Soc. America Proc. Vol. 38, pp 563-568.

Perry's Chemical Engineers' Handbook, 7th Ed. 1977. McGraw-Hill, New York, NY.

Radian Corporation. 1989. Short-Term Fate and Persistence of Motor Fuels in Soils. American Petroleum Institute Report DCN 89-204-145-04.

Schroeder, P. R., R. L. Peyton, B. M. McEnroe, and J. W. Sjostrom. 1989. The Hydrologic Evaluation of Landfill Performance (HELP) Model. Prepared for the U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.

Shan, C., and D. B. Stephens. 1995. An Analytical Solution for Vertical Transport of Volatile Chemicals in the Vadose Zone. J. of Contaminant Hydrology, Vol. 18, pp. 259-277.

Spencer, W. F., M. M. Cliath, W. A. Jury, and L. Z. Zhang. 1988. Volatilization of Organic Chemicals from Soil as Related to Their Henry's Law Constants. J. Environ. Qual., Vol. 17, no. 3, pp. 504-509.

Thibodeaux, L. J. 1981. Estimating the Air Emissions of Chemicals from Hazardous Waste Landfills. J. of Haz. Mat. No. 4. pp 235-244.

Toy, T. J., A. J. Kuhaida, Jr., and B. E. Munson. 1978. The prediction of mean monthly soil temperature from mean monthly air temperature, *Soil Science*, 126:181-189.

U.S. Environmental Protection Agency. 1988. Superfund Exposure Assessment Manual. Office of Solid Waste and Emergency Response, Washington, DC. EPA/540/1-88/001.

U.S. Environmental Protection Agency. 1989. Hazardous Waste Treatment, Storage, and Disposal

Facilities (TSDF) - Air Emission Models. Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-450/3-87-026.

U.S. Environmental Protection Agency. 1991. Air/Superfund National Technical Guidance Study Series, Database of Emission Rate Measurement Projects - Technical Note. Office of Air Quality Planning and Standards. Research Triangle Park, NC. EPA-450/1-91-003.

U.S. Environmental Protection Agency. 1992. Estimating the Potential for Occurrence of DNAPL at Superfund Sites. Office of Solid Waste and Emergency Response, Washington, D.C. Pub. 9355.4 - 07FS.

U.S. Environmental Protection Agency. 1995. *Review of Mathematical Modeling for Evaluating Soil Vapor Extraction Systems.* Office of Research and Development, Washington,. D.C. EPA/540/R-95-513.

U.S. Environmental Protection Agency. 1996. Soil Screening Guidance: Technical Background Document. Office of Emergency and Remedial Response, Washington, D.C. EPA/540/R95/128.

Walton, W. C. 1984. Practical Aspects of Groundwater Modeling. National Water Well Assoc., Worthington, Ohio.

APPENDIX A

EXAMPLE OF EMSOFT OUTPUT FILE FOR UNBURIED CONTAMINATION

EMSOFT INPUT PARAMETERS

OUTPUT FILE NAME: C:\EMSOFT\DATA\UNBURIED.OUT

CHEMICAL:	Benzene
KOC (ML/G):	5.8900E+01
KH (DIMENSIONLESS):	2.2800E-01
AIR DIFF COEFF (CM2/DAY):	7.6032E+03
AQU DIFF COEFF (CM2/DAY):	8.4672E-01
HALF LIFE (DAYS):	1.0000E+06
FRACTION ORG CARBON:	6.0000E-03
SOIL POROSITY:	4.3400E-01
SOIL WATER CONTENT:	1.5000E-01
SOIL BULK DENSITY (G/CM3):	1.5000E+00
EVAP(-)/INFILT(+) RATE (CM/DAY):	8.2000E-02
SURFACE BOUND LAYER (CM):	5.0000E-01
CLEAN COVER THICKNESS (CM):	0.0000E+00

LAYER THICKNESS (CM)	CONTAM CONC (MG/KG)
3.0000E+02	4.0000E+02

EMSOFT RESULTS

AVERAGE FLUX FOR 10950.000 DAYS

1.4672E-02

TIME (DAYS)	FLUX (MG/DAY/CM2):
0.25	9.2210E+00
109.75	2.7881E-01
219.25	1.2451E-01
328.75	7.3577E-02
438.25	4.9801E-02
547.75	3.6512E-02
657.25	2.8217E-02
766.75	2.2635E-02
876.25	1.8669E-02
985.75	1.5733E-02
1095.25	1.3488E-02
1204.75	1.1727E-02
1314.25	1.0315E-02
1423.75	9.1625E-03
1533.25	8.2077E-03
1642.75	7.4061E-03
1752.25	6.7254E-03
1861.75	6.1416E-03
1971.25	5.6365E-03
2080.75	5.1961E-03
2190.25	4.8092E-03
2299.75	4.4673E-03
2409.25	4.1634E-03

2518.75	3.8918E-03
2628.25	3.6479E-03
2737.75	3.4280E-03
2847.25	3.2289E-03
2956.75	3.0479E-03
3066.25	2.8828E-03
3175.75	2.7318E-03
3285.25	2.5931E-03
3394.75	2.4655E-03
3504.25	2.3478E-03
3613.75	2.2389E-03
3723.25	2.1379E-03
3832.75	2.0441E-03
3942.25	1.9568E-03
4051.75	1.8753E-03
4161.25	1.7991E-03
4270.75	1.7278E-03
4380.25	1.6609E-03
4489.75	1.5981E-03
4599.25	1.5390E-03
4708.75	1.4833E-03
4818.25	1.4308E-03
4927.75	1.3812E-03
5037.25	1.3343E-03
5146.75	1.2898E-03
5256.25	1.2477E-03
5365.75	1.2078E-03
5475.25	1.1698E-03
5584.75	1.1337E-03
5694.25	1.0994E-03
5803.75	1.0666E-03
5913.25	1.0354E-03
6022.75	1.0056E-03
6132.25	9.7717E-04
6241.75	9.4998E-04
6351.25	9.2396E-04
6460.75	8.9903E-04
6570.25	8.7517E-04
6679.75	8.5228E-04
6789.25	8.3033E-04
6898.75	8.0925E-04
7008.25	7.8901E-04
7117.75	7.6954E-04
7227.25	7.5082E-04
7336.75	7.3281E-04
7446.25	7.1546E-04
7555.75	6.9875E-04

7665.25	6.8264E-04
7774.75	6.6711E-04
7884.25	6.5213E-04
7993.75	6.3765E-04
8103.25	6.2368E-04
8212.75	6.1018E-04
8322.25	5.9713E-04
8431.75	5.8450E-04
8541.25	5.7229E-04
8650.75	5.6047E-04
8760.25	5.4903E-04
8869.75	5.3793E-04
8979.25	5.2719E-04
9088.75	5.1677E-04
9198.25	5.0667E-04
9307.75	4.9688E-04
9417.25	4.8736E-04
9526.75	4.7814E-04
9636.25	4.6919E-04
9745.75	4.6047E-04
9855.25	4.5202E-04
9964.75	4.4378E-04
10074.25	4.3579E-04
10183.75	4.2801E-04
10293.25	4.2044E-04
10402.75	4.1310E-04
10512.25	4.0592E-04
10621.75	3.9894E-04
10731.25	3.9215E-04
10840.75	3.8554E-04

DEPTH (CM)	AVERAGE CONC (MG/KG)
5.0000	4.8501E-01

TIME (DAYS)	AVERAGE CONC (MG/KG)
0.25	8.1807E+01
109.75	2.5293E+00
219.25	1.1295E+00
328.75	6.6751E-01
438.25	4.5181E-01
547.75	3.3125E-01
657.25	2.5599E-01
766.75	2.0535E-01
876.25	1.6937E-01
985.75	1.4273E-01
1095.25	1.2237E-01
1204.75	1.0639E-01
1314.25	9.3580E-02
1423.75	8.3126E-02

1533.25	7.4463E-02
1642.75	6.7191E-02
1752.25	6.1015E-02
1861.75	5.5719E-02
1971.25	5.1137E-02
2080.75	4.7141E-02
2190.25	4.3631E-02
2299.75	4.0529E-02
2409.25	3.7772E-02
2518.75	3.5308E-02
2628.25	3.3096E-02
2737.75	3.1100E-02
2847.25	2.9294E-02
2956.75	2.7652E-02
3066.25	2.6154E-02
3175.75	2.4784E-02
3285.25	2.3526E-02
3394.75	2.2369E-02
3504.25	2.1301E-02
3613.75	2.0313E-02
3723.25	1.9397E-02
3832.75	1.8545E-02
3942.25	1.7753E-02
4051.75	1.7014E-02
4161.25	1.6323E-02
4270.75	1.5676E-02
4380.25	1.5069E-02
4489.75	1.4499E-02
4599.25	1.3963E-02
4708.75	1.3458E-02
4818.25	1.2981E-02
4927.75	1.2531E-02
5037.25	1.2106E-02
5146.75	1.1703E-02
5256.25	1.1321E-02
5365.75	1.0958E-02
5475.25	1.0614E-02
5584.75	1.0286E-02
5694.25	9.9745E-03
5803.75	9.6776E-03
5913.25	9.3944E-03
6022.75	9.1241E-03
6132.25	8.8660E-03
6241.75	8.6192E-03
6351.25	8.3832E-03
6460.75	8.1571E-03
6570.25	7.9406E-03

6679.75	7.7330E-03
6789.25	7.5338E-03
6898.75	7.3426E-03
7008.25	7.1589E-03
7117.75	6.9823E-03
7227.25	6.8125E-03
7336.75	6.6490E-03
7446.25	6.4917E-03
7555.75	6.3401E-03
7665.25	6.1939E-03
7774.75	6.0530E-03
7884.25	5.9170E-03
7993.75	5.7857E-03
8103.25	5.6589E-03
8212.75	5.5364E-03
8322.25	5.4180E-03
8431.75	5.3035E-03
8541.25	5.1927E-03
8650.75	5.0854E-03
8760.25	4.9816E-03
8869.75	4.8810E-03
8979.25	4.7835E-03
9088.75	4.6890E-03
9198.25	4.5974E-03
9307.75	4.5085E-03
9417.25	4.4222E-03
9526.75	4.3385E-03
9636.25	4.2572E-03
9745.75	4.1782E-03
9855.25	4.1014E-03
9964.75	4.0268E-03
10074.25	3.9543E-03
10183.75	3.8837E-03
10293.25	3.8151E-03
10402.75	3.7483E-03
10512.25	3.6833E-03
10621.75	3.6200E-03
10731.25	3.5583E-03
10840.75	3.4983E-03

DEPTH (CM)	CONC (MG/KG)
0.00	5.4297E-05
0.10	1.8959E-04
0.20	3.2489E-04
0.30	4.6020E-04
0.40	5.9552E-04
0.50	7.3085E-04
0.60	8.6618E-04

0.70	1.0015E-03
0.80	1.1369E-03
0.90	1.2722E-03
1.00	1.4076E-03
1.10	1.5430E-03
1.20	1.6784E-03
1.30	1.8137E-03
1.40	1.9491E-03
1.50	2.0846E-03
1.60	2.2200E-03
1.70	2.3554E-03
1.80	2.4908E-03
1.90	2.6263E-03
2.00	2.7617E-03
2.10	2.8972E-03
2.20	3.0326E-03
2.30	3.1681E-03
2.40	3.3036E-03
2.50	3.4391E-03
2.60	3.5745E-03
2.70	3.7100E-03
2.80	3.8456E-03
2.90	3.9811E-03
3.00	4.1166E-03
3.10	4.2521E-03
3.20	4.3877E-03
3.30	4.5232E-03
3.40	4.6588E-03
3.50	4.7943E-03
3.60	4.9299E-03
3.70	5.0655E-03
3.80	5.2011E-03
3.90	5.3367E-03
4.00	5.4723E-03
4.10	5.6079E-03
4.20	5.7435E-03
4.30	5.8792E-03
4.40	6.0148E-03
4.50	6.1504E-03
4.60	6.2861E-03
4.70	6.4217E-03
4.80	6.5574E-03
4.90	6.6931E-03
5.00	6.8288E-03

APPENDIX B

EXAMPLE OF EMSOFT OUTPUT FILE FOR BURIED CONTAMINATION

EMSOFT INPUT PARAMETERS

OUTPUT FILE NAME: C:\EMSOFT\DATA\BURIED.OUT

CHEMICAL:	124 TRICHLOROBENZENE
KOC (ML/G):	1.7800E+03
KH (DIMENSIONLESS):	5.8200E-02
AIR DIFF COEFF (CM2/DAY):	2.5920E+03
AQU DIFF COEFF (CM2/DAY):	7.1107E-01
HALF LIFE (DAYS):	1.0000E+06
FRACTION ORG CARBON:	6.0000E-03
SOIL POROSITY:	4.3400E-01
SOIL WATER CONTENT:	1.5000E-01
SOIL BULK DENSITY (G/CM3):	1.5000E+00
EVAP(-)/INFILT(+) RATE (CM/DAY):	8.2000E-02
SURFACE BOUND LAYER (CM):	5.0000E-01
CLEAN COVER THICKNESS (CM):	5.0000E+01

LAYER THICKNESS (CM)	CONTAM CONC (MG/KG)
3.0000E+02	5.0000E+02

EMSOFT RESULTS

AVERAGE FLUX FOR 10950.000 DAYS

2.6515E-03

TIME (DAYS)	FLUX (MG/DAY/CM2):
0.25	0.0000E+00
109.75	1.4308E-05
219.25	4.5035E-04
328.75	1.2976E-03
438.25	2.1027E-03
547.75	2.7306E-03
657.25	3.1882E-03
766.75	3.5119E-03
876.25	3.7361E-03
985.75	3.8875E-03
1095.25	3.9857E-03
1204.75	4.0450E-03
1314.25	4.0755E-03
1423.75	4.0848E-03
1533.25	4.0783E-03
1642.75	4.0601E-03
1752.25	4.0331E-03
1861.75	3.9996E-03
1971.25	3.9614E-03
2080.75	3.9197E-03
2190.25	3.8756E-03
2299.75	3.8298E-03
2409.25	3.7829E-03

2518.75	3.7353E-03
2628.25	3.6876E-03
2737.75	3.6398E-03
2847.25	3.5923E-03
2956.75	3.5452E-03
3066.25	3.4986E-03
3175.75	3.4527E-03
3285.25	3.4075E-03
3394.75	3.3630E-03
3504.25	3.3193E-03
3613.75	3.2764E-03
3723.25	3.2343E-03
3832.75	3.1931E-03
3942.25	3.1527E-03
4051.75	3.1131E-03
4161.25	3.0744E-03
4270.75	3.0365E-03
4380.25	2.9993E-03
4489.75	2.9630E-03
4599.25	2.9275E-03
4708.75	2.8926E-03
4818.25	2.8586E-03
4927.75	2.8252E-03
5037.25	2.7925E-03
5146.75	2.7606E-03
5256.25	2.7292E-03
5365.75	2.6986E-03
5475.25	2.6685E-03
5584.75	2.6391E-03
5694.25	2.6102E-03
5803.75	2.5819E-03
5913.25	2.5542E-03
6022.75	2.5270E-03
6132.25	2.5004E-03
6241.75	2.4742E-03
6351.25	2.4486E-03
6460.75	2.4234E-03
6570.25	2.3987E-03
6679.75	2.3744E-03
6789.25	2.3506E-03
6898.75	2.3272E-03
7008.25	2.3042E-03
7117.75	2.2817E-03
7227.25	2.2595E-03
7336.75	2.2377E-03
7446.25	2.2163E-03
7555.75	2.1952E-03

7665.25	2.1745E-03
7774.75	2.1541E-03
7884.25	2.1341E-03
7993.75	2.1144E-03
8103.25	2.0950E-03
8212.75	2.0759E-03
8322.25	2.0571E-03
8431.75	2.0386E-03
8541.25	2.0203E-03
8650.75	2.0024E-03
8760.25	1.9847E-03
8869.75	1.9673E-03
8979.25	1.9502E-03
9088.75	1.9333E-03
9198.25	1.9166E-03
9307.75	1.9002E-03
9417.25	1.8841E-03
9526.75	1.8681E-03
9636.25	1.8524E-03
9745.75	1.8369E-03
9855.25	1.8216E-03
9964.75	1.8065E-03
10074.25	1.7916E-03
10183.75	1.7770E-03
10293.25	1.7625E-03
10402.75	1.7482E-03
10512.25	1.7341E-03
10621.75	1.7202E-03
10731.25	1.7064E-03
10840.75	1.6929E-03

DEPTH (CM)	AVERAGE CONC (MG/KG)
55.0000	7.4901E+01

TIME (DAYS)	AVERAGE CONC (MG/KG)
0.25	4.5441E+01
109.75	6.9474E+01
219.25	8.4664E+01
328.75	9.5133E+01
438.25	1.0240E+02
547.75	1.0737E+02
657.25	1.1067E+02
766.75	1.1275E+02
876.25	1.1392E+02
985.75	1.1442E+02
1095.25	1.1443E+02
1204.75	1.1406E+02
1314.25	1.1341E+02
1423.75	1.1255E+02

1533.25	1.1154E+02
1642.75	1.1041E+02
1752.25	1.0920E+02
1861.75	1.0794E+02
1971.25	1.0664E+02
2080.75	1.0531E+02
2190.25	1.0397E+02
2299.75	1.0263E+02
2409.25	1.0129E+02
2518.75	9.9964E+01
2628.25	9.8648E+01
2737.75	9.7349E+01
2847.25	9.6068E+01
2956.75	9.4807E+01
3066.25	9.3569E+01
3175.75	9.2352E+01
3285.25	9.1159E+01
3394.75	8.9990E+01
3504.25	8.8843E+01
3613.75	8.7721E+01
3723.25	8.6621E+01
3832.75	8.5545E+01
3942.25	8.4491E+01
4051.75	8.3460E+01
4161.25	8.2451E+01
4270.75	8.1463E+01
4380.25	8.0496E+01
4489.75	7.9549E+01
4599.25	7.8622E+01
4708.75	7.7715E+01
4818.25	7.6827E+01
4927.75	7.5957E+01
5037.25	7.5104E+01
5146.75	7.4270E+01
5256.25	7.3452E+01
5365.75	7.2650E+01
5475.25	7.1864E+01
5584.75	7.1094E+01
5694.25	7.0339E+01
5803.75	6.9598E+01
5913.25	6.8871E+01
6022.75	6.8158E+01
6132.25	6.7459E+01
6241.75	6.6772E+01
6351.25	6.6098E+01
6460.75	6.5436E+01
6570.25	6.4786E+01

6679.75	6.4147E+01
6789.25	6.3520E+01
6898.75	6.2903E+01
7008.25	6.2297E+01
7117.75	6.1702E+01
7227.25	6.1116E+01
7336.75	6.0540E+01
7446.25	5.9974E+01
7555.75	5.9417E+01
7665.25	5.8868E+01
7774.75	5.8329E+01
7884.25	5.7798E+01
7993.75	5.7276E+01
8103.25	5.6761E+01
8212.75	5.6254E+01
8322.25	5.5756E+01
8431.75	5.5264E+01
8541.25	5.4780E+01
8650.75	5.4303E+01
8760.25	5.3833E+01
8869.75	5.3370E+01
8979.25	5.2914E+01
9088.75	5.2464E+01
9198.25	5.2020E+01
9307.75	5.1583E+01
9417.25	5.1152E+01
9526.75	5.0726E+01
9636.25	5.0307E+01
9745.75	4.9893E+01
9855.25	4.9485E+01
9964.75	4.9082E+01
10074.25	4.8684E+01
10183.75	4.8292E+01
10293.25	4.7905E+01
10402.75	4.7522E+01
10512.25	4.7145E+01
10621.75	4.6773E+01
10731.25	4.6405E+01
10840.75	4.6041E+01

DEPTH (CM)	CONC (MG/KG)
0.00	6.0070E-02
1.10	1.7120E+00
2.20	3.3761E+00
3.30	5.0522E+00
4.40	6.7402E+00
5.50	8.4401E+00
6.60	1.0152E+01

7.70	1.1875E+01
8.80	1.3610E+01
9.90	1.5356E+01
11.00	1.7113E+01
12.10	1.8882E+01
13.20	2.0661E+01
14.30	2.2451E+01
15.40	2.4253E+01
16.50	2.6064E+01
17.60	2.7887E+01
18.70	2.9720E+01
19.80	3.1563E+01
20.90	3.3416E+01
22.00	3.5279E+01
23.10	3.7152E+01
24.20	3.9034E+01
25.30	4.0927E+01
26.40	4.2828E+01
27.50	4.4739E+01
28.60	4.6659E+01
29.70	4.8588E+01
30.80	5.0526E+01
31.90	5.2472E+01
33.00	5.4427E+01
34.10	5.6390E+01
35.20	5.8362E+01
36.30	6.0341E+01
37.40	6.2329E+01
38.50	6.4324E+01
39.60	6.6326E+01
40.70	6.8336E+01
41.80	7.0353E+01
42.90	7.2378E+01
44.00	7.4409E+01
45.10	7.6446E+01
46.20	7.8491E+01
47.30	8.0541E+01
48.40	8.2598E+01
49.50	8.4661E+01
50.60	8.6730E+01
51.70	8.8804E+01
52.80	9.0883E+01
53.90	9.2968E+01
55.00	9.5058E+01