EMSOFT User's Guide

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DISCLAIMER

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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, which was issued as a draft in 1993, provides 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. This 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. Efforts addressing these comments and suggestions are presented in the following document.

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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.

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 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 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 in 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 given 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, fraction 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.

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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 soil volume

J_s = Solute mass flux per unit soil area per unit time

μ = Net degradation rate

t = Time

z = Soil depth.

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

D_L = Soil-liquid diffusion coefficient

C_G = Concentration in the gas phase

C_L = Concentration in the liquid phase

J_w = Water flux.

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

$$D_G = \frac{a^{10/3}}{\phi^2} D_G^{air} \qquad (3)$$

where   a   = Soil air content

          ϕ = Soil porosity

          D_G = Air-gas diffusion coefficient.

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

$$D_L = \frac{\theta^{10/3}}{\phi^2} D_L^{water} \qquad (4)$$

where Θ = Volumetric water content

          D_L^{water} = Water-liquid diffusion coefficient.

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

$$C_T = \rho_b C_s + \theta C_L + a C_G \qquad (5)$$

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:

$$C_T = R_s C_s = R_L C_L = R_G C_G \qquad (6)$$

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:

$$-D_E \frac{\partial C_T}{\partial z} + V_E C_T = -H_E C_T \; , \qquad for \; z = 0 \tag{15}$$

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:

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

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

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

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

where erfc is the complementary error function.

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

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

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

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

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:

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

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.

o   <u>Steady porewater flux</u>. 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.

o   <u>Homogeneous soil properties</u>. 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.

o   <u>Chemicals present in dissolved form at low concentrations</u>. The equilibrium partitioning relationships used in the model are no longer valid when a pure phase of a chemical or mixture of chemicals or high dissolved concentrations are present. Thus, the model should not be applied in situations where a pure chemical phase exists.

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.

°   <u>Volatilization at the surface occurs through a stagnant air boundary layer of thickness d</u>. 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 11 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 on a 3.5" diskette. To install the model on the hard drive of your computer, insert the model disk into the disk drive, and from the directory or subdirectory in which you want the program to reside, type COPY [drive]:*.* <ENTER>, where [drive] is the drive in which the disk was inserted (generally A or B). This will copy the contents of the model disk into the current directory or subdirectory. Forty-nine files are on the disk, 46 of which are required to run EMSOFT:

- °   EMSOFT.BAT
- °   MSOFT.EXE
- °   DISPLAY.COM
- °   BEG.COM
- °   END.COM
- °   41 files with AID extension.

The 47th file (EMSOFT.FOR) is the Fortran code on which the model is based. The last two files are example chemical properties for benzene (BENZENE.CHM) and an example simulation data file (BENZENE.DAT). The model can be run directly from a floppy disk or from

the hard disk. Run times will be faster from a hard disk. To run the model, type: EMSOFT
<ENTER>. 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.

IMPORTANT NOTE: If Microsoft WINDOWS is loaded on your PC and the mouse is
not operable when running EMSOFT from the DOS prompt, reload
your mouse driver with a setup option that includes DOS.

With the keyboard, cursor movement is controlled by the arrow keys and the <ENTER> key. In
general, the left arrow key and the up arrow key move the cursor to the previous input field in a
screen, while the right arrow key and down arrow key move the cursor to the next input field in a
screen. Due to programming constraints, in some screens (those with scroll bars), the up and
down arrow keys do not move the cursor from one field to another. In this case, the right and left
arrow keys must be used. The <ENTER> key moves the cursor to the next input field in a
screen.

Most of the screens have an OK button and a CANCEL button. A button can be
"pressed" by positioning the cursor on it and pressing <ENTER> or <F10>, or by clicking the
mouse button. Pressing the OK button validates the choices and input parameters entered on the
screen. It causes control to be transferred to the next model screen; therefore, the user should be
satisfied with the selections made before proceeding. Pressing the CANCEL button allows the
user to terminate execution of the model, and return to the DOS prompt. To prevent accidental
model termination, the user is requested to confirm that model termination is in fact desired.
Model execution can also be aborted at any time by pressing the <ESC> key.

The input screens also have a BACKUP 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 OK, go to the next screen, and then back up two screens.

3.3   MESSAGE BARS AND HELP SCREENS

Message bars appear at the bottom of each screen. The message displayed provides information related to the input field at which the cursor is positioned. Generally, it consists of a brief instruction to aid the user. More detailed information can be obtained by calling up the help screen related to the item.

On-line help screens are available to describe many selection options and input parameters. The help screen is displayed by positioning the cursor on the item for which help is needed and pressing the <F1> key. A help screen will be displayed for the item, offering a short description and instructions. To leave the help screen and return to the current model screen, press <F1> again.

3.4   SCREEN DESCRIPTIONS

The 11 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: Restart/quit.

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

```
┌─────────────────────────────────────────────────┐
│ ┌─────────────────────────────────────────────┐ │
│ │  ┌──────────────────────────────────────┐    │ │
│ │  │            E M S O F T               │    │ │
│ │  │ Exposure Model for Soil-Organic Fate │ V. 1.3 │
│ │  │         and Transport                │  6/96 │ │
│ │  └──────────────────────────────────────┘    │ │
│ │                                                │ │
│ │  Developed by ENSR Consulting and Engineering, Acton, MA, │
│ │  for U.S. EPA, National Center for Environmental Assessment, │
│ │  Washington, DC, based on codes provided by W. Jury, U. of CA, │
│ │  Riverside, CA                                 │ │
│ │        ) ) ) ) ) ) ) ) ) ) ) ) ) ) )          │ │
│ │        ( ( ( ( ( ( ( ( ( ( ( ( ( ( (          │ │
│ │  ██████████████████████████████████            │ │
│ │                                                │ │
│ │  ██████████████████████████████████            │ │
│ │                                                │ │
│ │           ┌──────────┐                         │ │
│ │           │    OK    │                         │ │
│ │           └──────────┘                         │ │
│ └─────────────────────────────────────────────┘ │
│     PRESS <ENTER>, <F10>, OR CLICK HERE TO CONTINUE │
└─────────────────────────────────────────────────┘
```

SCREEN 1: Title

```
┌─────────────────────────────────────────────────┐
│ ┌─────────────────────────────────────────────┐ │
│ │             I N P U T   O P T I O N S        │ │
│ │                                                │ │
│ │ ▓ USE AN EXISTING FILE FOR INPUT  ┌────────┬──┐│ │
│ │   OF LAYER, SOIL PARAMETER, AND   │FILENAME:│↑ ││ │
│ │   CHEMICAL-SPECIFIC DATA          │  FOR   │███││ │
│ │                                   │ALL DATA│███││ │
│ │                                   │ INPUT  │↓ ││ │
│ │                                   ├────────┼──┤│ │
│ │ ▓ USE AN EXISTING FILE FOR INPUT OF│FILENAME:│↑ ││ │
│ │   OF CHEMICAL-SPECIFIC DATA ONLY, │  FOR   │███││ │
│ │   OR TO OVERRIDE ABOVE CHEMICAL-  │CHEMICAL│███││ │
│ │   SPECIFIC DATA INPUTS            │  DATA  │███││ │
│ │                                   │ INPUT  │↓ ││ │
│ │                                   └────────┴──┘│ │
│ │       ┌──────────┐      ┌──────────┐           │ │
│ │       │    OK    │      │  CANCEL  │           │ │
│ │       └──────────┘      └──────────┘           │ │
│ └─────────────────────────────────────────────┘ │
│          PRESS <SPACEBAR> TO TOGGLE YES/NO        │
└─────────────────────────────────────────────────┘
```

SCREEN 2: Input Options

```
              C A L C U L A T I O N   O P T I O N S

     ☐  TIME-AVERAGED FLUX   ☐  TIME- AND DEPTH-AVERAGED SOIL CONCENTRATION

     ☐  FLUX v TIME          ☐  DEPTH-AVERAGED SOIL CONCENTRATION v TIME

                            ☐  SOIL CONCENTRATION v DEPTH

              C A L C U L A T I O N   C O N T R O L

     TIME PERIOD FOR AVERAGING AND PRINTING
     FLUX AND SOIL CONCENTRATION RESULTS                :        (DAYS)

     DEPTH (D1) FOR AVERAGING SOIL CONCENTRATION RESULTS:        (CM)

     DEPTH (D2) FOR PRINTING SOIL CONCENTRATION RESULTS :        (CM)


                  ┌────────┐    ┌──────┐    ┌────────┐
                  │ BACKUP │    │  OK  │    │ CANCEL │
                  └────────┘    └──────┘    └────────┘

     VALUE OUT OF RANGE ⇒DISPLAY,IP,=  0.0000000000000000E+000⇐=
```

SCREEN 3: Output Control and Calculation Options

```
                  C H E M I C A L   D A T A

     CHEMICAL NAME                            :

     ORGANIC CARBON PARTITION COEFFICIENT (ML/G):

     HENRY'S LAW CONSTANT (DIMENSIONLESS)     :

     AIR DIFFUSION COEFFICIENT (CM2/DAY)      :

     AQUEOUS DIFFUSION COEFFICIENT (CM2/DAY)  :

     HALF LIFE (DAYS)                         :

     NUMBER OF LAYERS OF CONTAMINATION        :

     ☐  SAVE ABOVE DATA IN THE FILE           :


                  ┌────────┐    ┌──────┐    ┌────────┐
                  │ BACKUP │    │  OK  │    │ CANCEL │
                  └────────┘    └──────┘    └────────┘

     ENTER THE CHEMICAL NAME (MAX 25 CHARACTERS) (PRESS F1 FOR HELP)
```

SCREEN 4: Chemical Data

```
                    S O I L   P R O P E R T I E S
FRACTION ORGANIC CARBON (DIMENSIONLESS)  :

POROSITY (DIMENSIONLESS)                 :

WATER CONTENT (DIMENSIONLESS)            :

BULK DENSITY (G/CM3)                     :

                 P H Y S I C A L   C O N S T A N T S

POREWATER FLUX (CM/DAY) (-=UP, +=DOWN)   :

BOUNDARY LAYER THICKNESS (CM)            :


              [ BACKUP ]    [ OK ]    [ CANCEL ]


   INPUT THE SOIL FRACTION ORGANIC CARBON (PRESS F1 FOR HELP)
```

SCREEN 5: Soil Properties and Physical Constants

```
                    L A Y E R   P R O P E R T I E S
                      COVER      LAYER     CONTAMINANT
                    THICKNESS  THICKNESS  CONCENTRATION
                      (CM)       (CM)        (MG/KG)

        COVER
        LAYER 1
        LAYER 2
        LAYER 3




              [ BACKUP ]    [ OK ]    [ CANCEL ]

   INPUT COVER THICKNESS (0 FOR NO COVER) (PRESS F10 TO VALIDATE SCREEN)
```

SCREEN 6: Layer Properties

17

```
            ┌──────────────────────────────────────────┐
            │                                          │
            │          I N P U T   S A V E             │
            │                                          │
            │   ┌─┐                                    │
            │   │ │ SAVE ALL INPUT DATA IN THE FILE:    │
            │   └─┘                                    │
            │                                          │
            │          O U T P U T   S A V E           │
            │                                          │
            │   ┌─┐                                    │
            │   │ │ SAVE ALL OUTPUTS IN THE FILE:       │
            │   └─┘                                    │
            │       B E G I N   C A L C U L A T I O N S │
            │                                          │
            │    ┌────────┐  ┌──────┐  ┌────────┐       │
            │    │ BACKUP │  │  OK  │  │ CANCEL │       │
            │    └────────┘  └──────┘  └────────┘       │
            │                                          │
            └──────────────────────────────────────────┘
             PRESS <SPACE> OR CLICK ON THIS BOX TO SAVE ALL INPUT DATA IN A FILE
```

SCREEN 7: Input/Output Save

```
            ┌──────────────────────────────────────────┐
            │                                          │
            │                                          │
            │                                          │
            │              ┌──────────────────┐        │
            │              │ CALCULATING...   │        │
            │              │                  │        │
            │              │ Please be Patient │        │
            │              └──────────────────┘        │
            │                                          │
            │                                          │
            │                                          │
            └──────────────────────────────────────────┘
```

SCREEN 8: Calculation Screen

18
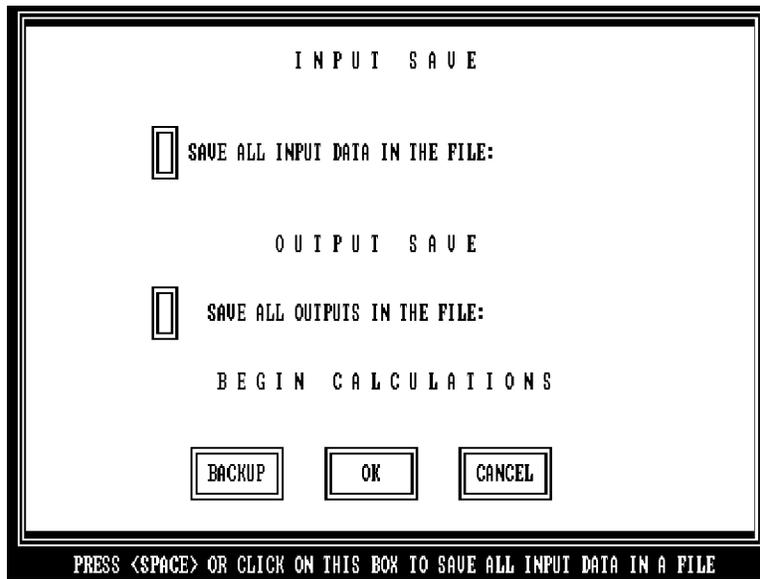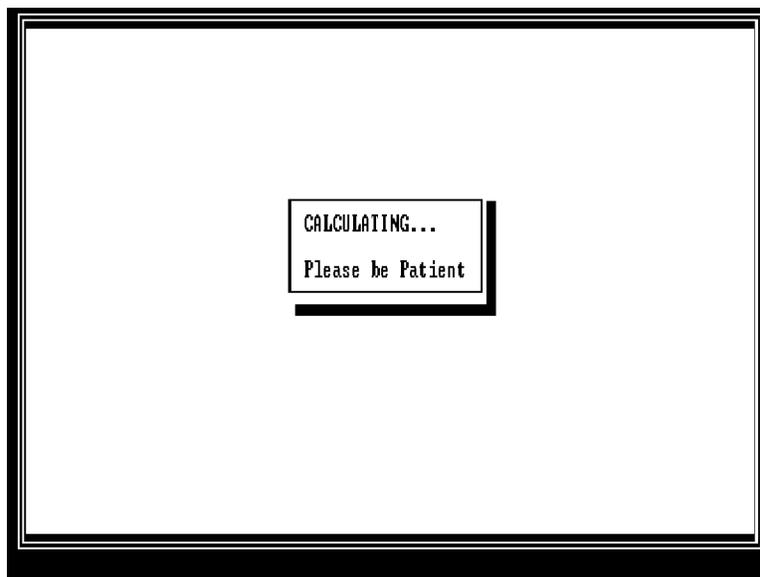
```
 ┌─────────────────────────────────────────────────────────┐
 │              M O D E L   O U T P U T S - F L U X          │
 │                                                           │
 │   ┌────────┬────────────┐   ┌───────────────────────────┐│
 │   │ TIME   │SURFACE FLUX│   │ AVERAGE SURFACE FLUX       ││
 │   │ (DAYS) │(MG/DAY/CM2)│   │                           ││
 │   ├────────┼────────────┤   │              MG/DAY/CM2    ││
 │ ↑ │        │            │   │ FOR A DURATION OF          ││
 │   │        │            │   │                           ││
 │   │        │            │   │              DAYS          ││
 │   │        │            │   └───────────────────────────┘│
 │   │        │            │                                 │
 │   │        │            │                                 │
 │   │        │            │            ┌─────────┐          │
 │ ↓ │        │            │            │   OK    │          │
 │   └────────┴────────────┘            └─────────┘          │
 │  USE UP AND DOWN ARROW KEYS TO SCROLL THROUGH MODEL OUTPUT│
 └─────────────────────────────────────────────────────────┘
```

SCREEN 9: Flux Results

```
 ┌──────────────────────────────────────────────────────────────────┐
 │          M O D E L   O U T P U T S - C O N C E N T R A T I O N     │
 │                                                                    │
 │ ┌──────┬──────────┐ ┌──────┬──────────┐ ┌────────────────────────┐ │
 │ │DEPTH │  SOIL    │ │ TIME │AVERAGE SOIL│ │AVERAGE SOIL            │ │
 │ │ (CM) │CONCENTRA-│ │(DAYS)│CONCENTRA- │ │CONCENTRATION           │ │
 │ │      │TION      │ │      │TION       │ │                        │ │
 │ │      │(MG/KG)   │ │      │(MG/KG)    │ │              MG/KG      │ │
 │ ├──────┼──────────┤↑├──────┼──────────┤↑│ OVER A DEPTH OF         │ │
 │ │      │          │ │      │          │ │                        │ │
 │ │      │          │ │      │          │ │              CM         │ │
 │ │      │          │ │      │          │ │ FOR A DURATION OF       │ │
 │ │      │          │ │      │          │ │                        │ │
 │ │      │          │ │      │          │ │              DAYS       │ │
 │ │      │          │↓│      │          │↓└────────────────────────┘ │
 │ │      │          │ │      │          │  ┌─────────┐ ┌─────────┐   │
 │ └──────┴──────────┘ └──────┴──────────┘  │PREVIOUS │ │   O     │   │
 │                                          │ SCREEN  │ │   K     │   │
 │                                          └─────────┘ └─────────┘   │
 │    USE UP AND DOWN ARROW KEYS TO SCROLL THROUGH OUTPUT DATA         │
 └──────────────────────────────────────────────────────────────────┘
```

SCREEN 10: Soil Concentration Results

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```
                    R E S T A R T




        ┌──────────┐          ┌──────────┐
        │    OK    │          │   QUIT   │
        └──────────┘          └──────────┘




  PRESS <ENTER>, <F10>, OR CLICK HERE TO START ANOTHER MODEL RUN
```
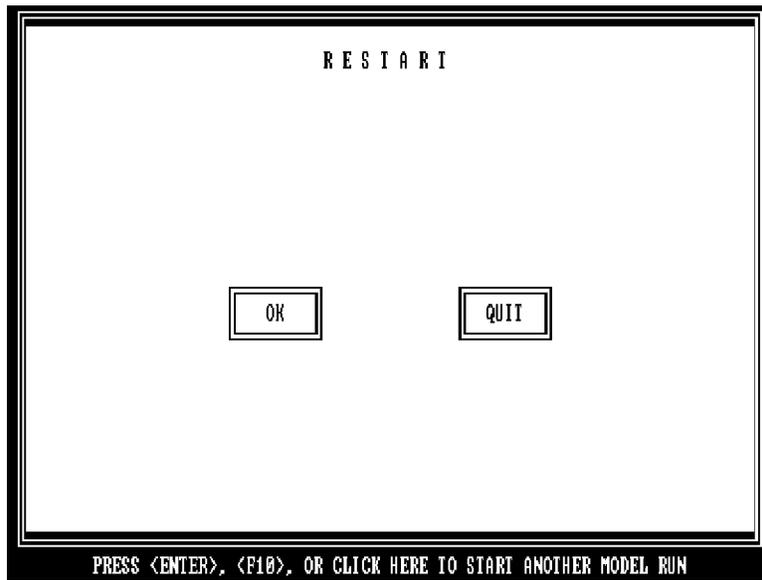
SCREEN 11: Restart/Quit

Below, each screen is described sequentially, 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 OK 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. The first option - use of an existing file for all of the soil parameters, chemical properties, and layer information - is selected by clicking the mouse on the box to the left of the text or pressing the space bar. An asterisk will appear in the box if this option is selected. It can be de-selected by clicking the mouse or pressing the space bar again. Available files (those having a .DAT file extension) are displayed in the region to the right of the option. The user moves the cursor to this region using the right arrow or <ENTER> key. The user can then scroll through this list using the up and down arrow keys, and select the desired file by clicking the mouse on it or pressing <ENTER>. A maximum of 15 .DAT files will be displayed.

The second option - use of an existing file to give 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 .CHM file extension) are shown in the region to the right of the option. A maximum of 15 .CHM files will be displayed.

These options offer several useful features. Using the first option, a given problem 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 f_{oc} 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 analysis. 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.

IMPORTANT NOTE: All input data files (.DAT and .CHM) created during a given session are not available for reuse after the model calculations have been performed unless the program has been exited and restarted.

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 cursor on the option box and pressing <ENTER>, the space bar, or clicking the mouse. 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 99,999.9 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 99 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 but may only be accessed after exiting and restarting the program. 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 $\log(K_{ow})$:

$$logK_{oc} = 3.95 - 0.62logS \tag{20}$$

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

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 (8.21×10^{-5} atm-m^3/gmol-°K), and T is the temperature at standard conditions in °K.

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 4320 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. The TTN system operator telephone number is (919) 541-4814. The TTN is also available through the world wide web at "http://ttnwww.rtpnc.epa.gov."

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:

$$C = C_O \exp(-\mu t) \tag{23}$$

where C is the concentration at time t, C_o is the initial concentration, and μ is the decay constant, equal to $\ln2/t_{1/2}$. 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 999,999 days.

Table 3-1 gives the range of acceptable values for the chemical data when running the EMSOFT model. Values entered outside of these ranges will result in a system error.

TABLE 3-1. VALUE RANGES FOR CHEMICAL DATA

Chemical parameter	Units	Acceptable range
Organic carbon partition coefficient	ml/g	1.00E-02 - 1.00E+09
Henry's law constant	(dimensionless)	1.00E-10 - 999
Air diffusion coefficient	(cm^2/day)	10 - 10,000
Aqueous diffusion coefficient	(cm^2/day)	0.01 - 10
Half life	(days)	1 - 999,999

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 (n or 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 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 ground

water transport to the surface during the dry season. Eagleson (1978) presents the following
equation to calculate this evaporation rate:

$$E = K_{sat}\left[1 + \frac{3/2}{mc-1}\right]\left[\frac{\Psi_{sat}}{Z}\right]^{mc} for \ \frac{E}{E_{pot}} < 1 \qquad (24)$$

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:

$$m = \frac{2}{c-3}. \qquad (25)$$

Guidance on the selection of c is provided by Table 3-2. Guidance on the selection of
representative soil hydraulic parameters is provided by Table 3-3.

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

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TABLE 3-2. 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 3-3. 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.		

consult the cited references for further information. As an indication of the feasible rangeof potential evapotranspiration rates, measured values are provided in Table 3-4.

TABLE 3-4. OBSERVED VALUES OF ANNUAL POTENTIAL EVAPORTRANSPIRATION

Location	Observed E_{pot}, in/yr
Mesilla, N.M.	34.0
Pecos, N.M.	35.3
Sangamon R., Ill.	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)	

Boundary Layer Thickness--

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

$$d \; = \; \frac{D_{wv}^{air} \; \rho_{wv} \; (1 \; - \; RH)}{2E\rho_{WL}} \tag{26}$$

where $D_{wv}{}^{air}$ = Is the binary diffusion coefficient of water vapor in air

ρ_{wv} = Is the saturated water vapor density

RH   = Is the relative humidity

E   = Is the evaporation rate

ρ_{WL} = Is the 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):

$$d = \frac{26v}{V_* Sc^{1/3}}$$ (27)

where v = Is the kinematic viscosity of air (about 1.5×10^5 m^2/s)

V_* = Is the friction velocity

Sc = Is the Schmidt number.

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

$$V_* = 0.01V(6.1 + 0.63V)^{0.5}$$ (28)

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

Typical values for boundary layer thickness were calculated using Equations 27 and 28 with a range of windspeeds. These calculations are summarized in Table 3-5, 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 3-5. BOUNDARY LAYER THICKNESSES FOR DIFFERENT WINDSPEEDS

Windspeed, m/s	Boundary layer thickness, cm	
	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 3-6 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 27 and 28. Calculations by Jury et al. (1984c) using Equation 26 are also in general agreement with the values shown in Table 3-6. A default boundary layer thickness that may be used in EMSOFT when no other data are available is 0.5 cm.

Table 3-7 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.

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

TABLE 3-6. 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 3-7. 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

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 can be saved in files 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, options are selected by pressing the space bar, <ENTER>, or clicking the mouse. 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. Files saved during a particular model run cannot be reaccessed until exiting and restarting the program.

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 the up and down arrow keys. The page up and page down keys can also be used, but may not reveal all of the values. Therefore, use the arrow keys to access the remaining values.

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 final screen.

3.4.11 <u>Screen 11: Restart</u>

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 quit option can be selected to terminate execution of the model. To retrieve input files saved during the model run, quit the program and then restart by typing EMSOFT <ENTER>.

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

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 (μg/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).
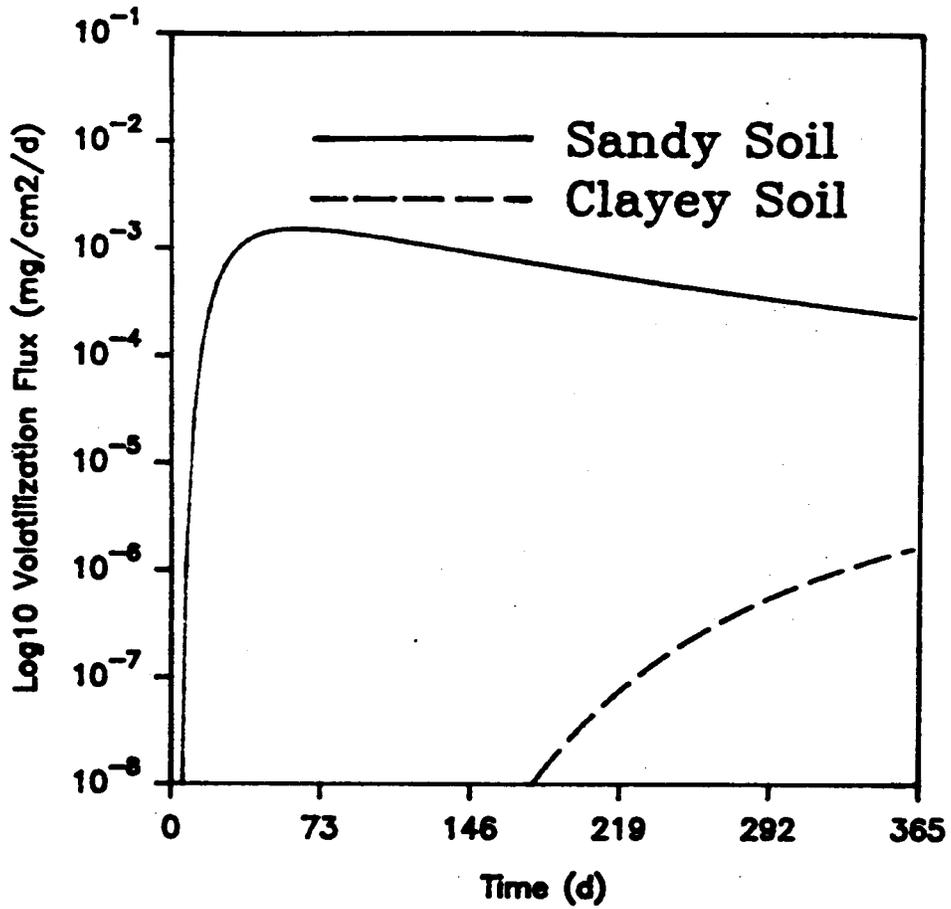
Figure 4-1. Flux versus time for benzene calculated by EMSOFT.
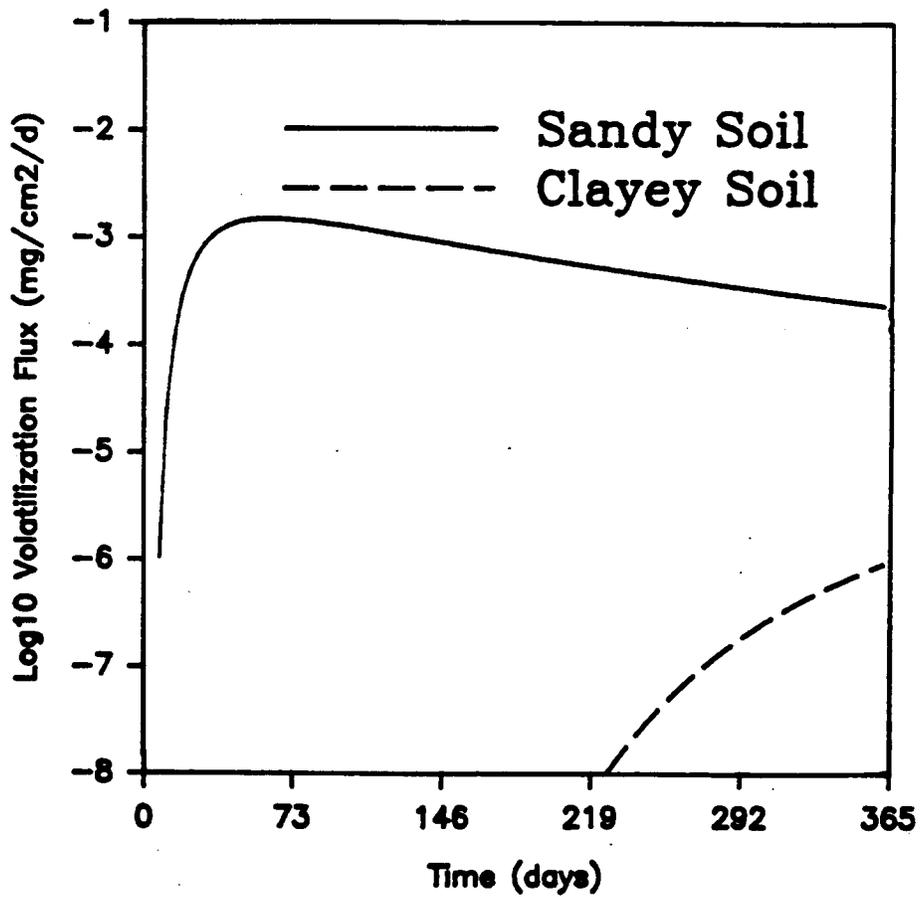
Figure 4-2. Flux versus time for benzene calculated by SCREENB.
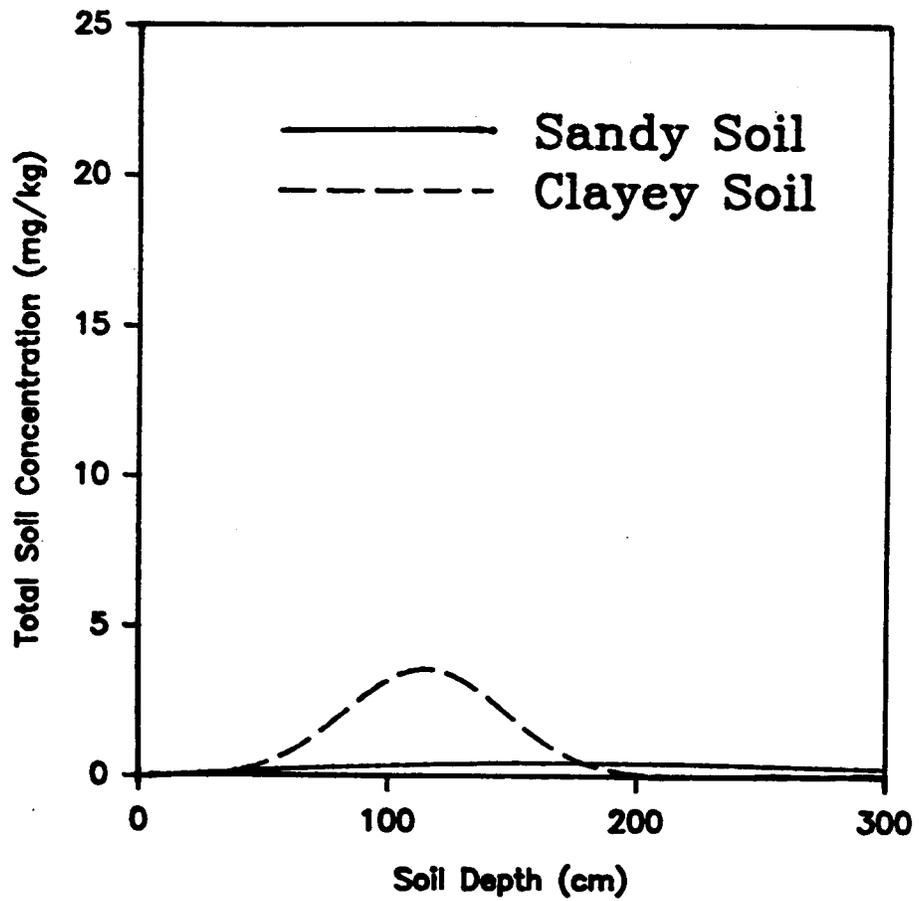
Figure 4-3. Concentration versus depth for benzene calculated by EMSOFT.
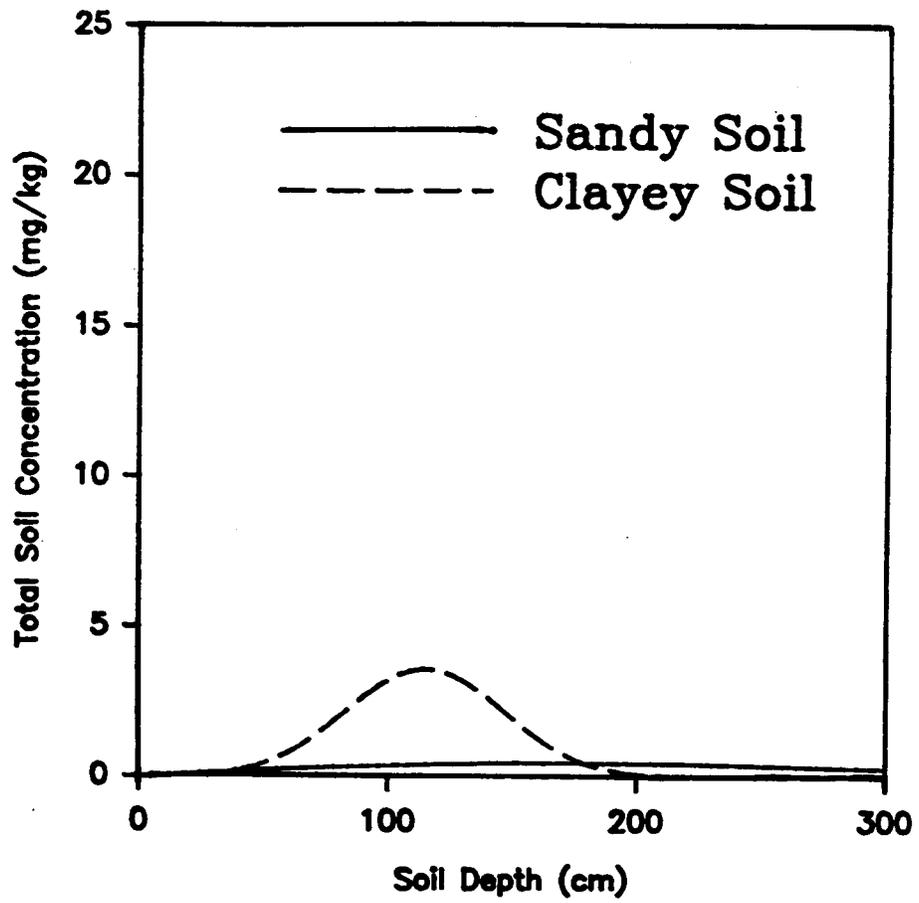
Figure 4-4. Concentration versus depth for benzene calculated by SCREENB.
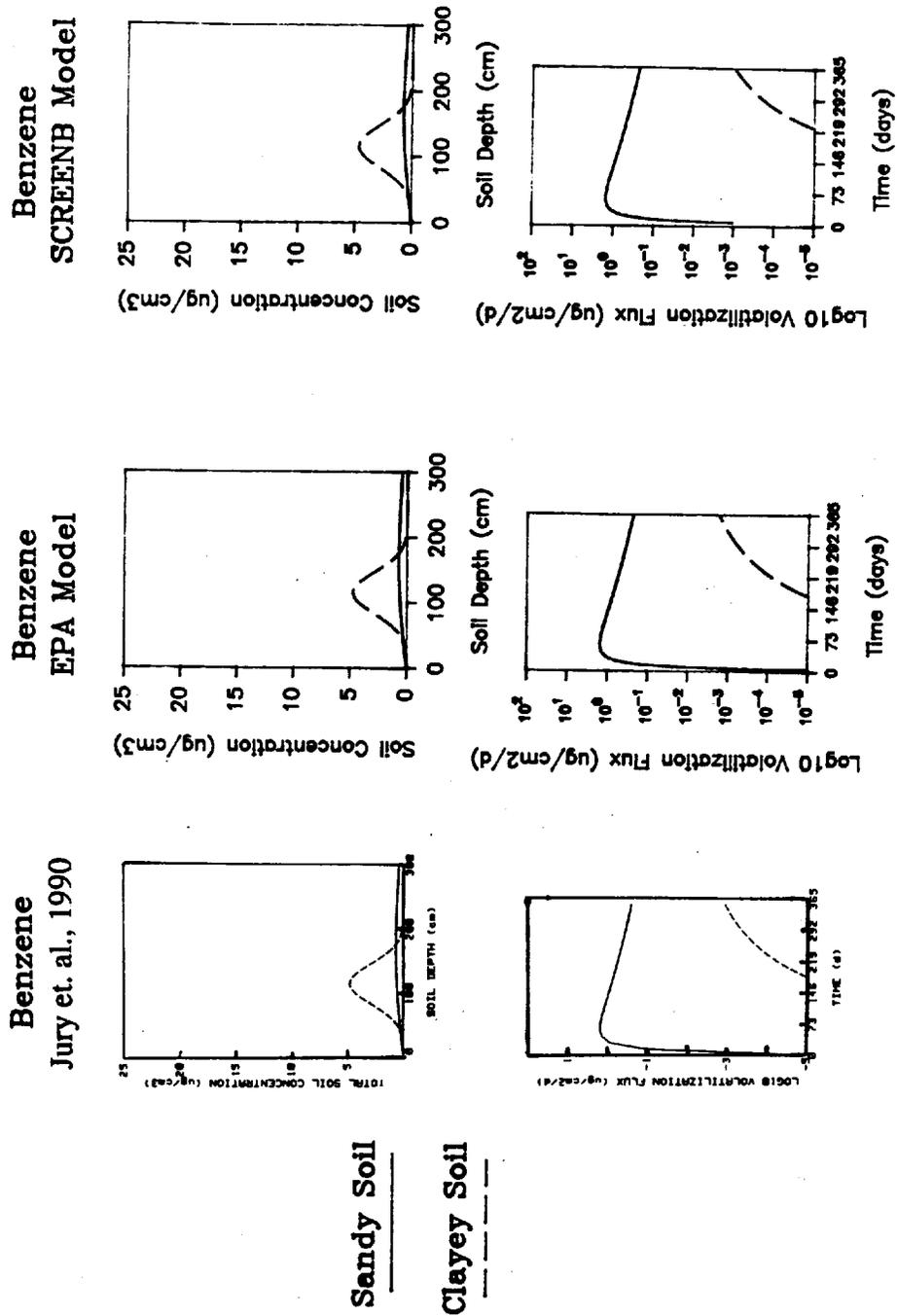
Figure 4-5. Comparison of surface flux and concentration results from Jury et al.

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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.

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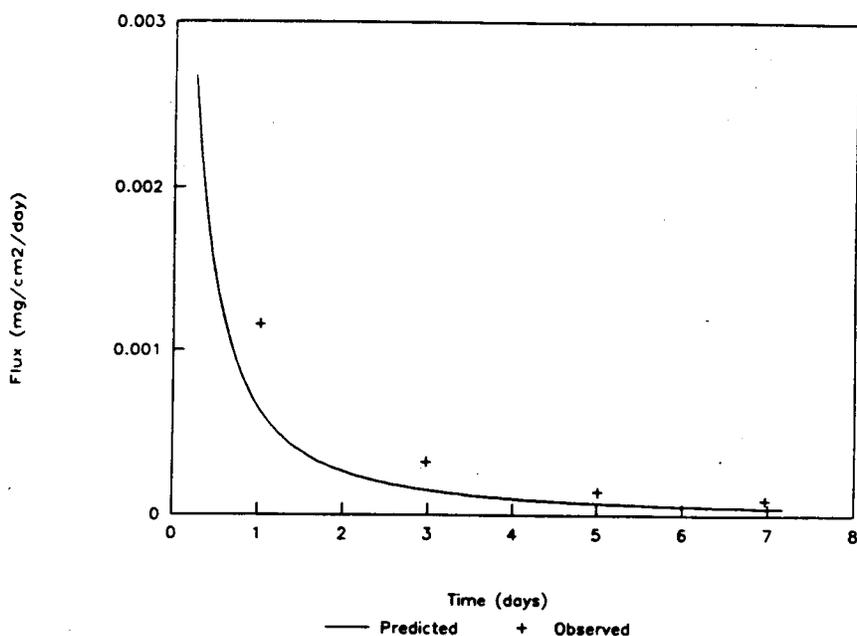
Figure 5-1a. Predicted and observed lindane flux, Farmer 10 mg/kg - base case.

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.

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
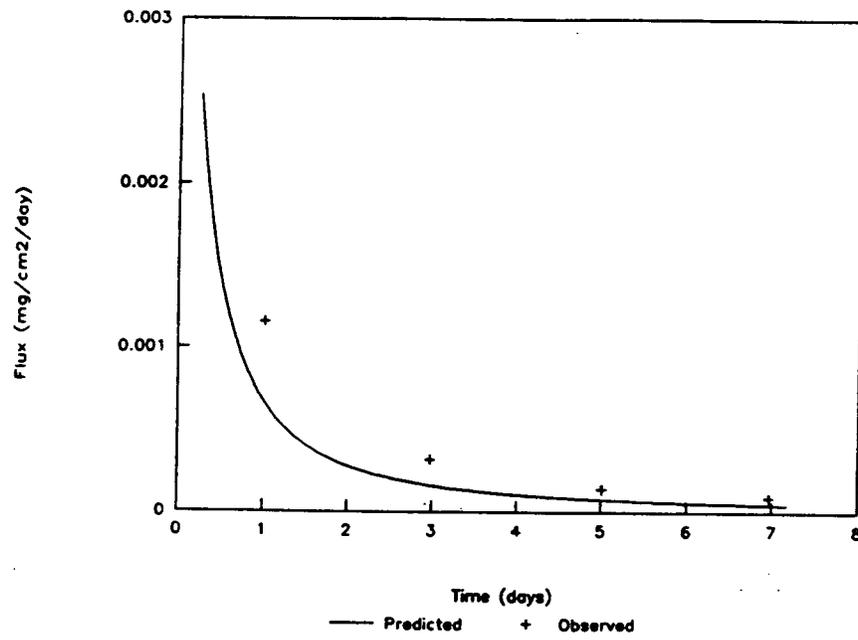
Figure 5-1b. Predicted and observed lindane flux, Farmer 10 mg/kg - K_{oc} = 1300 ml/g.
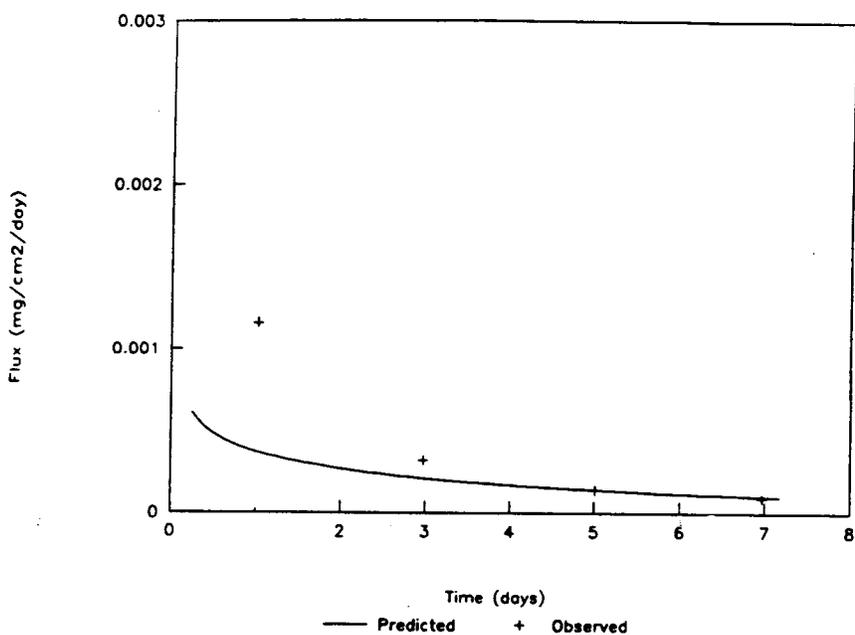
Figure 5-1c. Predicted and observed lindane flux, Farmer 10 mg/kg - K_H = 2.23-05.

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).

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.

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.

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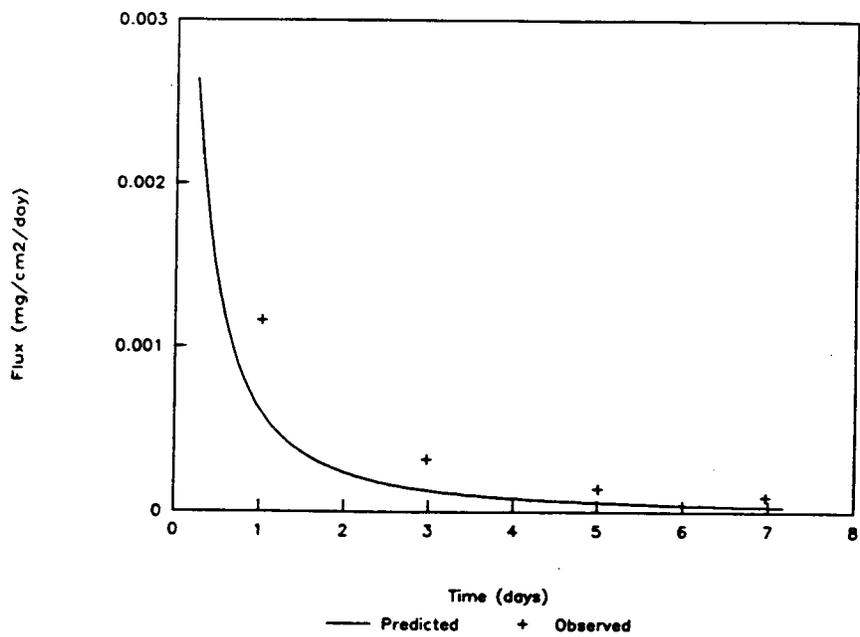
Figure 5-1d. Predicted and observed lindane flux, Farmer 10 mg/kg - half life = 14 days.
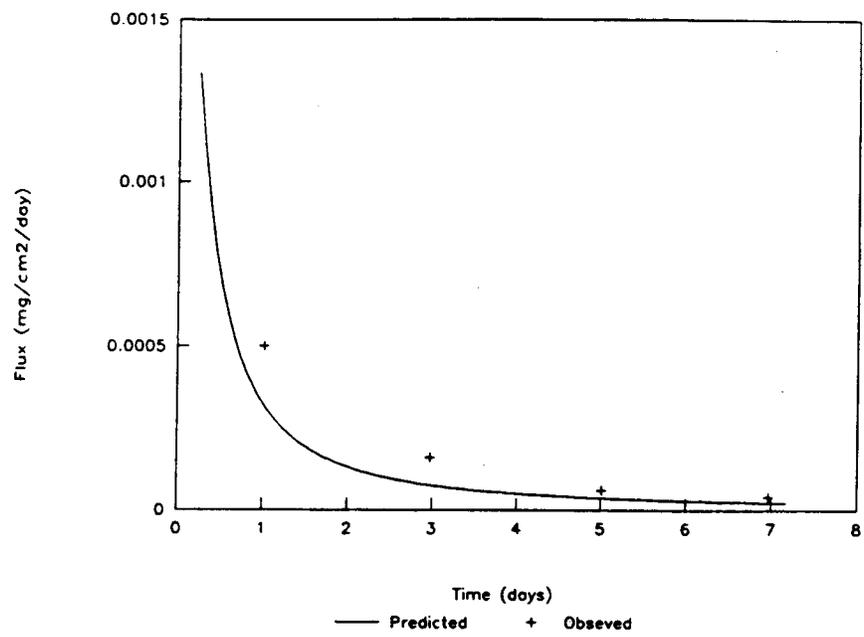
Figure 5-2. Predicted and observed lindane flux, Farmer 5 mg/kg.
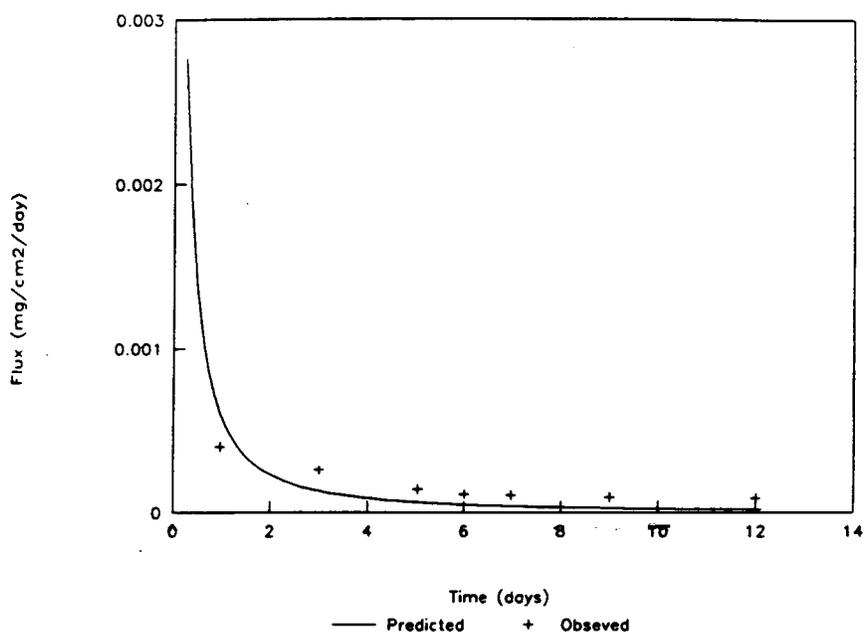
Figure 5-3a. Predicted and observed dieldrin flux, Farmer 10 mg/kg - base case.

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.

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 5-4 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.

60
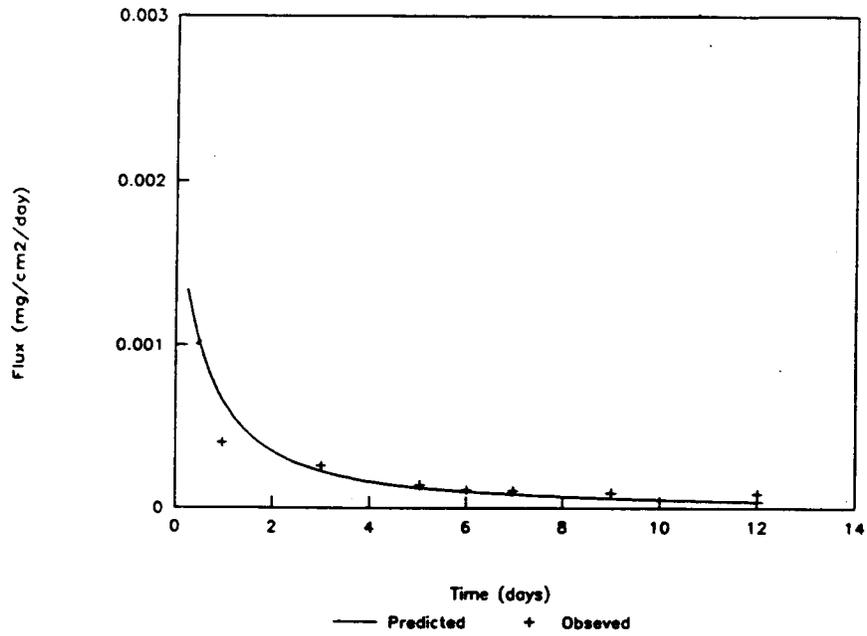
Figure 5-3b. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_{oc} = 12,000 ml/g.

61
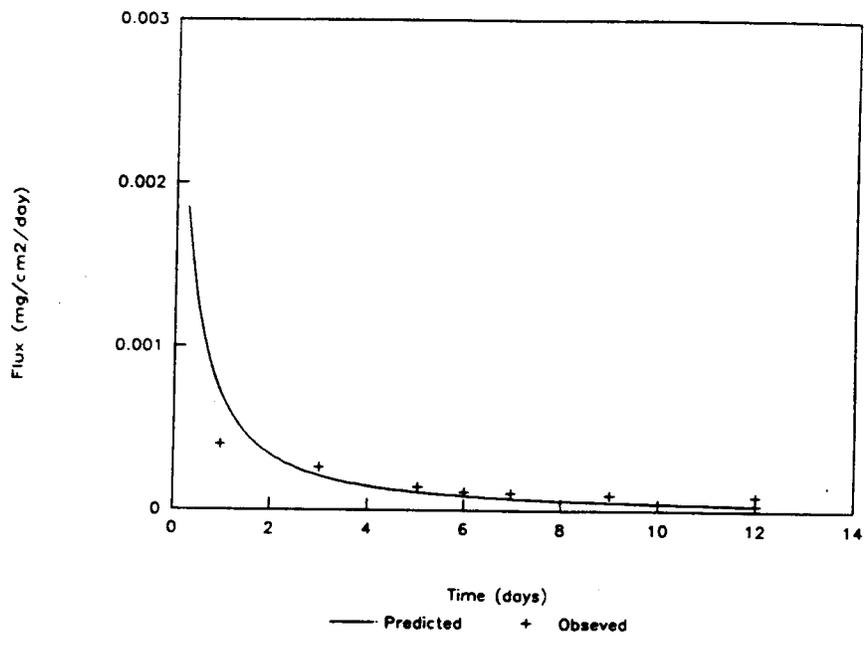
Figure 5-3c. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_H = 6.7e-04.
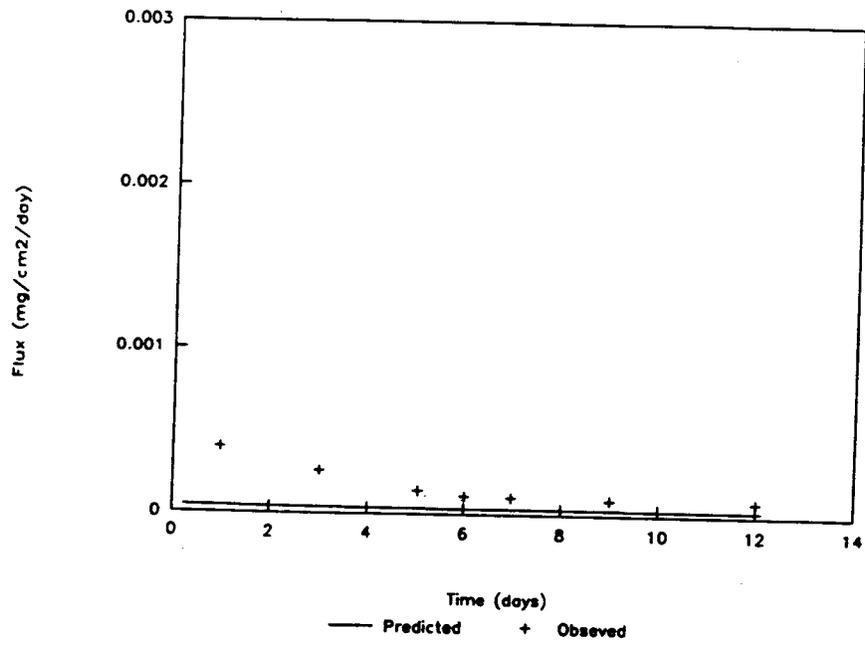
Figure 5-3d. Predicted and observed dieldrin flux, Farmer 10 mg/kg - K_H = 8.9e-06.
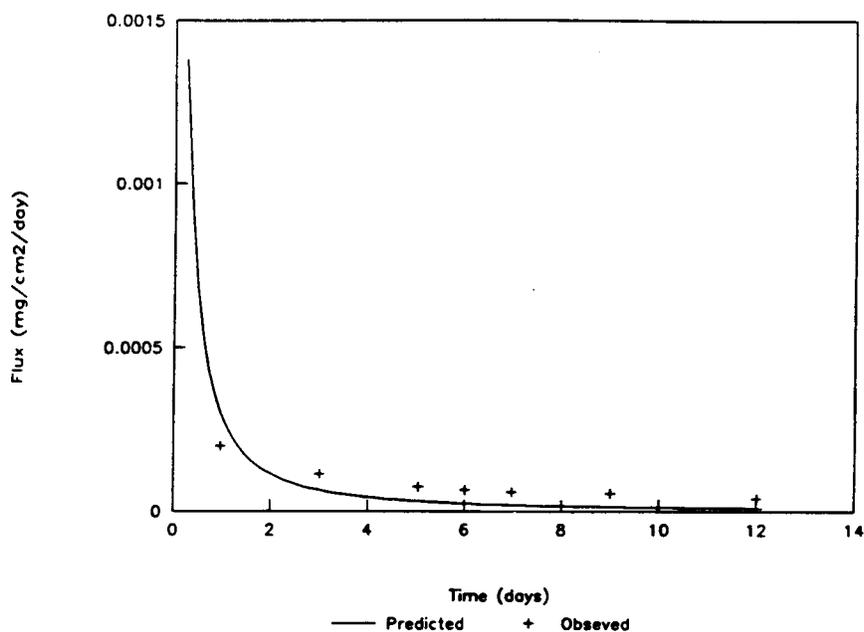
Figure 5-4. Predicted and observed dieldrin flux, Farmer 5 mg/kg.

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. 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 underpredicted emission fluxes by 13 percent at day 21 and by 37 percent at day 29.

64
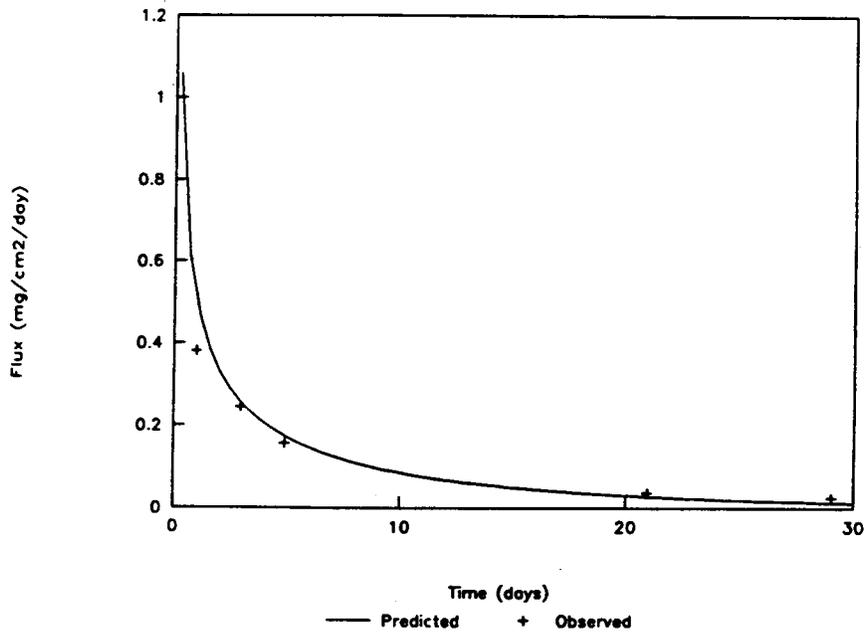
Figure 5-5. Predicted and observed ethyl benzene flux, Radian 310 mg/kg.
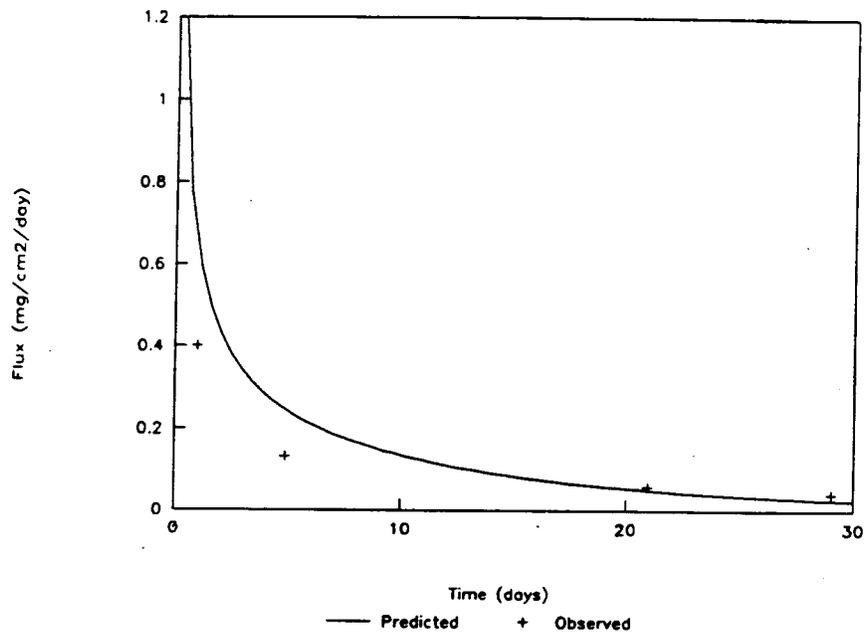
Figure 5-6a. Predicted and observed benzene flux, Radian 110 mg/kg - base case.

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.

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).

66
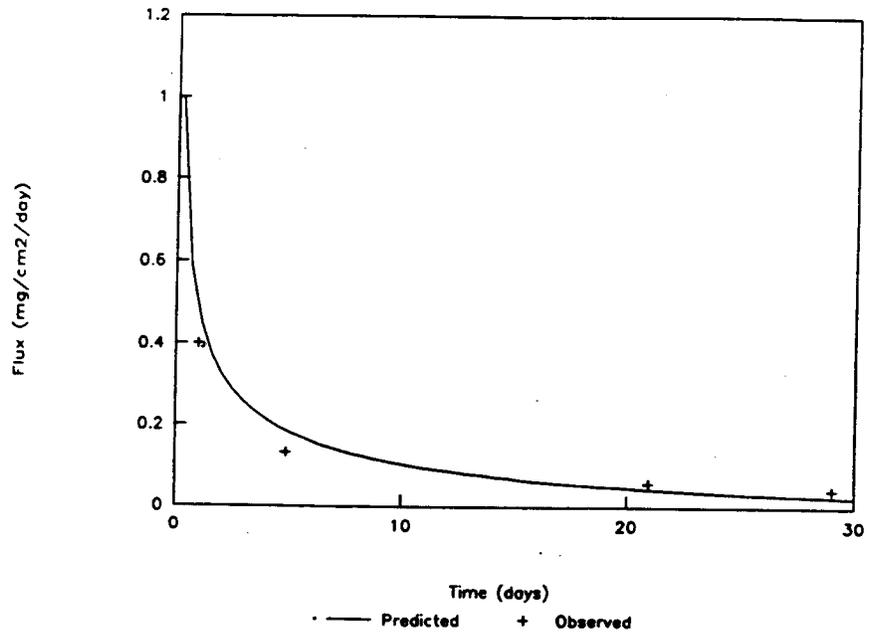
Figure 5-6b. Predicted and observed benzene flux, Radian 110 mg/kg - default diffusion coefficients.
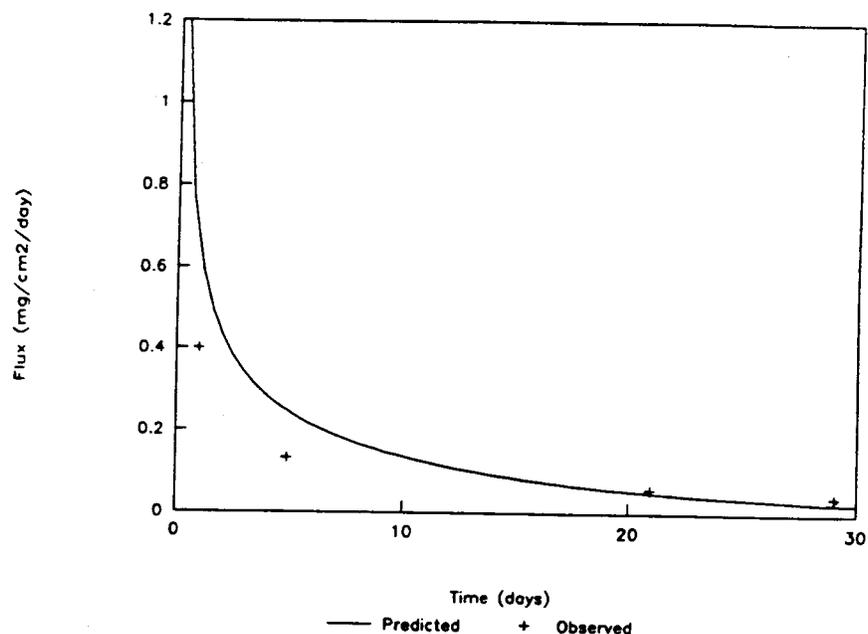
Figure 5-6c. Predicted and observed benzene flux, Radian 110 mg/kg - boundary layer = 1.5 cm.

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).
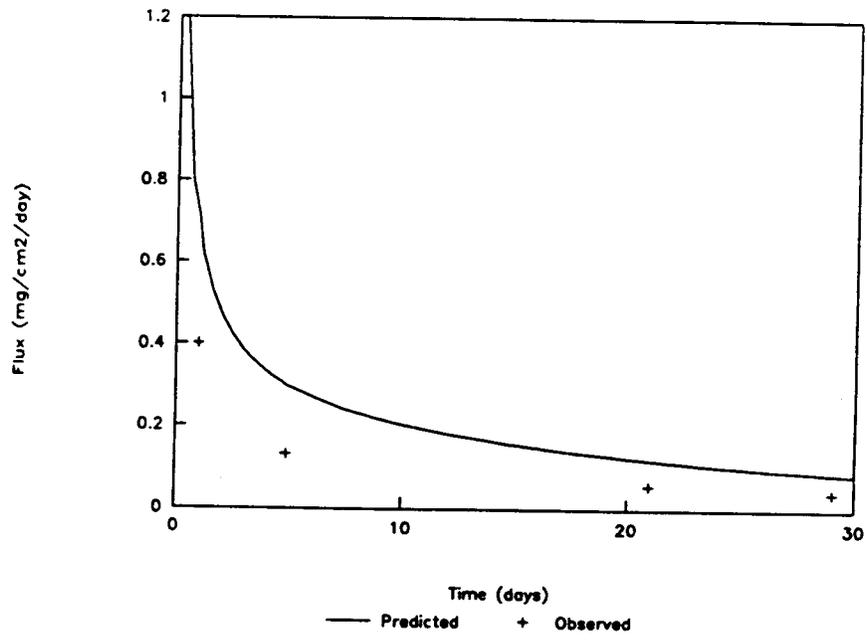
Figure 5-6d. Predicted and observed benzene flux, Radian 110 mg/kg - half life = 365 days.
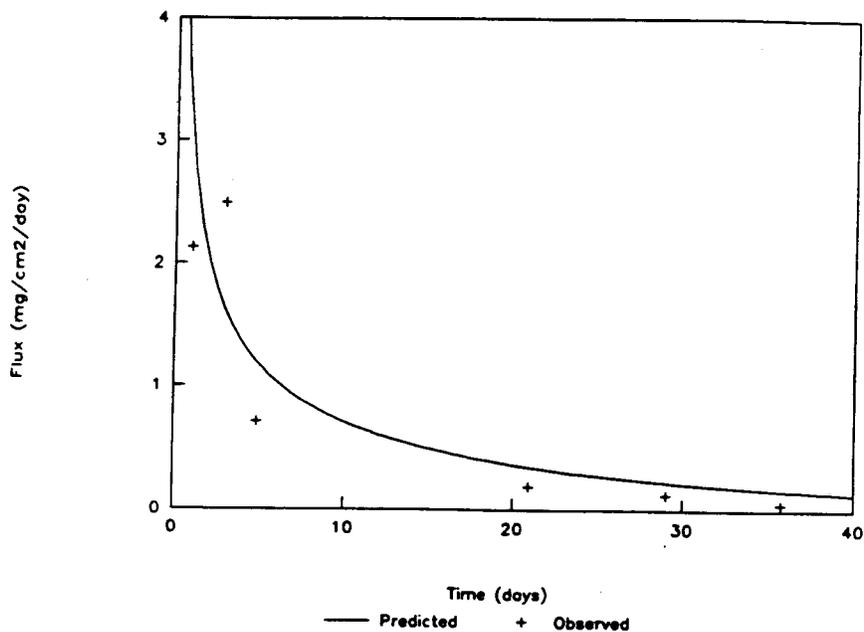
Figure 5-7. Predicted and observed toluene flux, Radian 880 mg/kg.

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.

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.

70
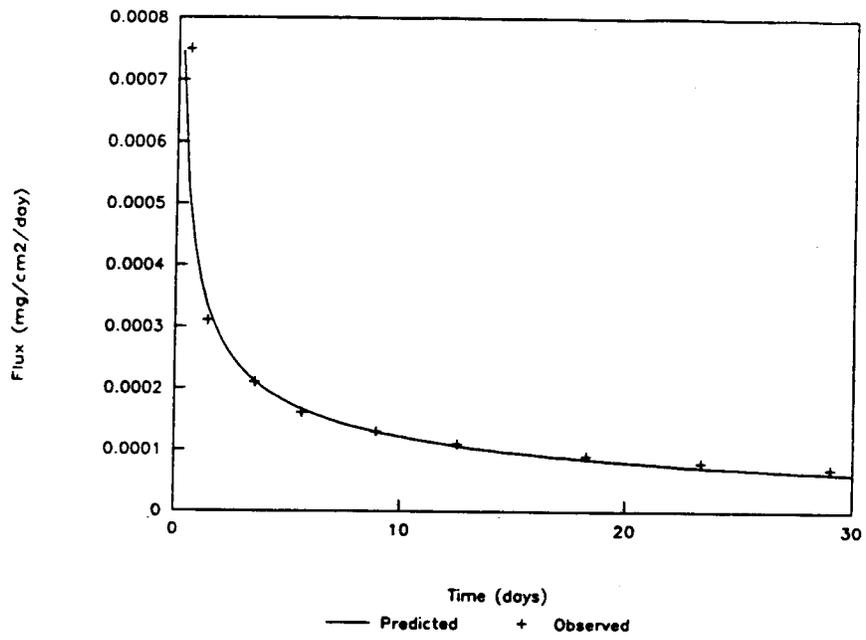
Figure 5-8. Predicted and observed triallate flux, Jury 10 mg/kg.
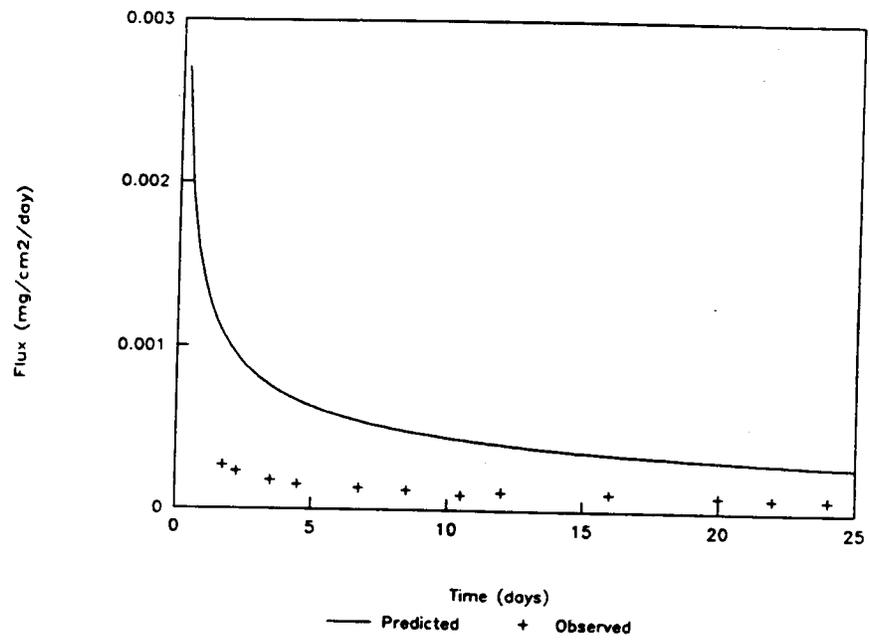
Figure 5-9a. Predicted and observed dieldrin flux, Spencer & Cliath 10 mg/kg - boundary layer = 1.2 cm.
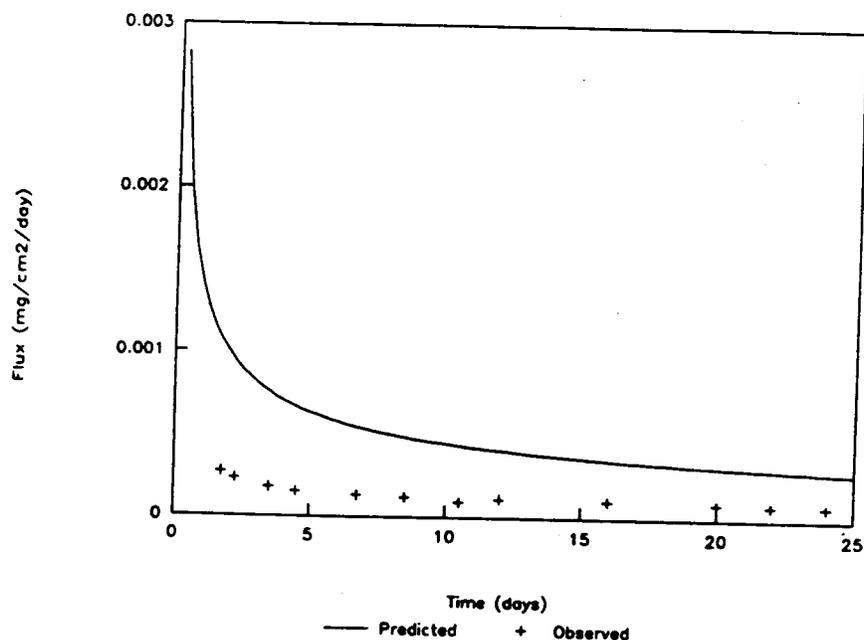
Figure 5-9b. Predicted and observed dieldrin flux, Spencer & Cliath 10 mg/kg - boundary layer = 0.12 cm.

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.

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

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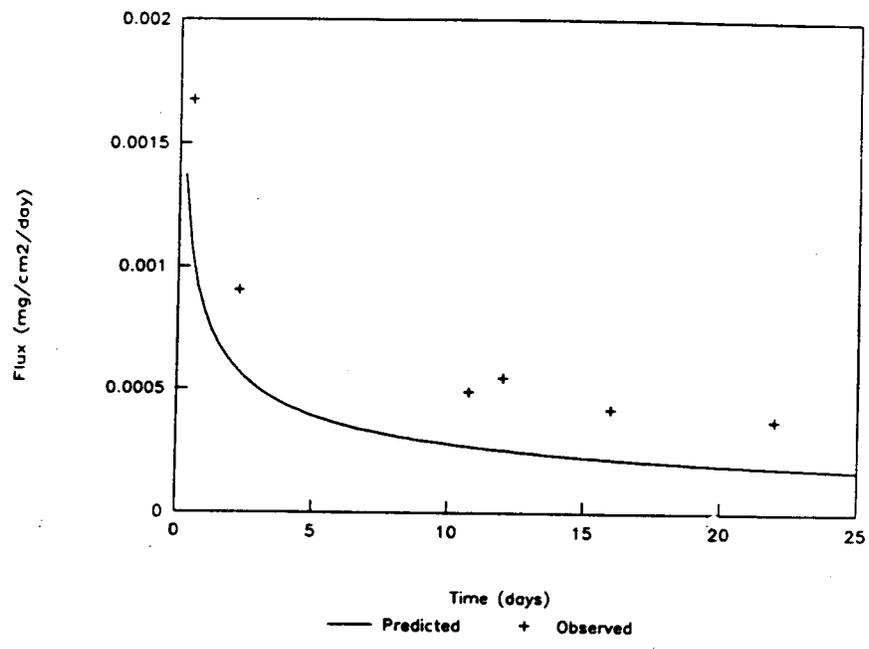
Figure 5-10. Predicted and observed lindane flux, Spencer & Cliath 10 mg/kg.

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

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.

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

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APPENDIX A

EXAMPLE OF EMSOFT OUTPUT FILE FOR UNBURIED CONTAMINATION

EMSOFT INPUT PARAMETERS

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):
    .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
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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
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7117.75 7.6954E-04
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7336.75 7.3281E-04
7446.25 7.1546E-04

```
7555.75  6.9875E-04
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7993.75  6.3765E-04
8103.25  6.2368E-04
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8322.25  5.9713E-04
8431.75  5.8450E-04
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9417.25  4.8736E-04
9526.75  4.7813E-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)
```
  .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
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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
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5146.75 1.1703E-02
5256.25 1.1321E-02
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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
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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)
   .00  5.4297E-05
   .10  1.8959E-04
   .20  3.2489E-04
```

.30 4.6020E-04
.40 5.9552E-04
.50 7.3085E-04
.60 8.6618E-04
.70 1.0015E-03
.80 1.1369E-03
.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

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):
    .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)

```
   .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)
   .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