Mathematical models that predict the contamination potential of chemical inputs on the soil surface or in the upper unsaturated soil zone are an increasingly important and useful management tool. Mathematical models can be formulated by following physically based and system approaches. In this study, models based on these approaches were developed to simulate Fenamiphos transport in highly aggregated Hawaiian Oxic soils. Concentration profiles calculated with these models showed rather close similarity to and agreement with measured profiles. Conjunctive use of these models revealed their intrinsic relationship and the consistency between them.
AUTHORS:

Dr. Clark C.K. Liu
Professor
Department of Civil Engineering
University of Hawaii at Manoa
2540 Dole Street
Honolulu, Hawaii 96822
Tel.: 808/956-7658

Dr. Keith Loague
Assistant Professor of Soil and
Wildland Hydrology
Department of Soil Science
108 Hilgard Hall
University of California
Berkeley, California 94720
Tel.: 415/643-5327

Mr. Wei Chen
1388 Kapiolani Boulevard, 2nd Floor
Fukunaga & Associates, Inc.
Honolulu, Hawaii 96814
Tel.: 808/944-1821

Mr. Jing-Song Feng
Graduate Student
Department of Civil Engineering
University of Hawaii at Manoa
2540 Dole Street
Honolulu, Hawaii 96822

Mr. Qin-Ming Huang
Graduate Student
Department of Civil Engineering
University of Hawaii at Manoa
2540 Dole Street
Honolulu, Hawaii 96822
SIMULATION OF SOLUTE TRANSPORT IN HETEROGENEOUS SOILS
VOLUME I: Conjunctive Application of Physically Based and
System Modeling Approaches

Clark C.K. Liu
Keith Loague
Wei Chen
Jing-Song Feng
Qin-Ming Huang

Special Report 06.30:91(I)

June 1991

PREPARED FOR
U.S. Geological Survey
Project Completion Report
for
"Compatibility of Physically Based and Linear System Solute
Transport Modeling Approaches and Their Conjunctive Application"
Project No.: 14-08-001-G1489
Principal Investigator: Clark C.K. Liu
Co-Investigator: Keith Loague

The contents of this report were developed under a grant from the Department of the Interior,
U.S. Geological Survey. However, those contents do not necessarily represent the policy of that
agency, and you should not assume endorsement by the Federal Government.

WATER RESOURCES RESEARCH CENTER
University of Hawaii at Manoa
Honolulu, Hawaii 96822
ABSTRACT

Mathematical models that predict the contamination potential of chemical inputs on the soil surface or in the upper unsaturated soil zone are an increasingly important and useful management tool. Mathematical models can be formulated by following physically based and system approaches. In this study, models based on these approaches were developed to simulate Fenamiphos transport in highly aggregated Hawaiian Oxic soils. Concentration profiles calculated with these models showed rather close similarity to and agreement with measured profiles. Conjunctive use of these models revealed their intrinsic relationship and the consistency between them.
CONTENTS

ABSTRACT ........................................................................................................... v
INTRODUCTION ................................................................................................. 1
LINEAR SYSTEM MODEL OF SOLUTE TRANSPORT IN SOILS ......................... 3
SYSTEM IDENTIFICATION TECHNIQUES ....................................................... 4
APPLICATION OF PHYSICAL PARAMETERIZATION METHOD ......................... 5
APPLICATION OF SYSTEM PARAMETERIZATION METHOD ............................. 18
CONJUNCTIVE USE OF GREY-BOX AND WHITE-BOX METHODS .................. 28
DISCUSSION ....................................................................................................... 34
CONCLUSIONS ................................................................................................... 35
REFERENCES CITED ........................................................................................... 37

Figures

1. Physically Based Modeling Approach ................................................................. 2
2. System Modeling Approach ............................................................................... 3
3. Revised Two-Component Solute Transport Model ........................................... 7
4. A Typical Impulse Response Function for Revised Two-Component Solute Transport Model ................................................................. 9
5. Simulation of Solute Transport in Upper Soil by a System Modeling Approach ................................................................. 10
6. Impulse Response Functions of Five Soil-Solute Systems ................................. 15
7. Fenamiphos Concentration Distribution in Soil at 10-cm Depth, Kunia Site .......... 15
8. Fenamiphos Concentration Distribution in Soil at 20-cm Depth, Kunia Site .......... 16
9. Fenamiphos Concentration Distribution in Soil at 30-cm Depth, Kunia Site .......... 16
10. Fenamiphos Concentration Distribution in Soil at 40-cm Depth, Kunia Site .......... 17
11. Fenamiphos Concentration Distribution in Soil at 50-cm Depth, Kunia Site .......... 17
12. Fenamiphos Concentration Distribution in Soil as Measured and Computed by a White-Box Model at 396 days, Kunia Site ......................... 19
13. Fenamiphos Concentration Distribution in Soil at 24 days, Kunia Site .......... 24
14. Fenamiphos Concentration Distribution in Soil at 96 days, Kunia Site .......... 25
15. Fenamiphos Concentration Distribution in Soil at 205 days, Kunia Site .......... 25
16. Fenamiphos Concentration Distribution in Soil as Measured and Computed by a Grey-Box Model at 396 days, Kunia Site ................................. 26
INTRODUCTION

Agricultural chemicals developed to enhance production and/or control undesirable pests have been extensively used throughout the country because of their effectiveness and economic feasibility. On the other hand, the residuals of all the applied chemicals might be able to enter the groundwater aquifers, which happen to be our main water source. Such processes as volatilization, chemical and biological decay, percolation, and diffusion and dispersion control the fate and distribution of the applied chemicals leaching in the soil, as well as in groundwater aquifers.

Because of the extremely high cost of measuring the temporal and spatial distribution of the chemical concentration in soils and aquifers, mathematical modeling of the dynamic nature of the aforementioned processes is very much desired as an alternative for analysis and prediction.

A lot of effort has been put into the study of the fate of various chemicals. The classic mathematical model is the so-called convection-dispersion equation (for a saturated flow regime):

$$\frac{\partial C}{\partial t} + U \cdot \nabla C = \nabla (D \nabla C),$$  \hspace{1cm} (1)

where \(C\) is the concentration, \(t\) is time, \(U\) is flow velocity, and \(D\) is the dispersion tensor, which shows a distinct scale dependence caused by the heterogeneity of the media. If the flow regime is unsaturated, the equation will include water content; the velocity field \(U\) is also affected by water content. The one-dimensional equation takes the following form:

$$C(h) \frac{\partial h}{\partial t} = \left\{ \frac{\partial}{\partial z} \left[ K(h) \frac{\partial h}{\partial z} \right] \right\} - \frac{\partial K(h)}{\partial z} + \Phi,$$  \hspace{1cm} (2)

where \(C(h) = \partial \theta(h) / \partial h\) is the water capacity or the slope of the soil water retention curve \(\theta(h)\), \(z\) is downward distance, \(K\) is the hydraulic conductivity, and \(\Phi\) the sources and sinks of water. More terms need to be added into the equations if decay, sorption, desorption, and other processes are not negligible. Because of the complexity and difficulties in dealing with heterogeneity and its effect on the hydrodynamic parameters, assumption of homogeneity is usually made in applying these models, then attempts are made to obtain a closer approximation of the real situation. Stochastical differential equations have been used to handle the scale effect of dispersion tensor caused by heterogeneity (Gelhar and Axness 1983; Gelhar, Gutjahr, and Naff 1979). However, primarily due to the assumption of stationarity, the effectiveness and the representativeness of this approach are still under debate. The spatial heterogeneity of field soils produces a scale effect that is hard to incorporate into such a model (Sposito, Jury, and Gupta 1986; Wheatcraft and Tyler 1988).
Recently, attention has been paid to preferential flow and to the solute transport phenomenon in structured or aggregated soils. By conceptualizing soil water as being partitioned into mobile and immobile parts, and positing an exchange of concentrations between these two parts in a nonequilibrium situation, the so-called two-region and two-site models seem to produce better results than the classical convection-dispersion equation (Nielsen, Van Genuchten, and Biggar 1986; Van Genuchten and Wierenga 1976; Van Genuchten and Dalton 1986).

All these types of models are called physically based ones because they try to model all the intimate physical mechanisms occurring in the media-solute system. This approach is illustrated as a flow chart in Figure 1. It is not difficult to see that this approach has some inherent weaknesses. The most significant weaknesses are: (1) justifications of specific forms of conceptual formulation are hard to establish; (2) each model parameter must be determined independently by laboratory and field experiments, which are often difficult to conduct; and (3) the governing equation of a physically based transport model with complex initial and boundary conditions is usually not solvable analytically.

Modeling the solute transport in soil can be accomplished alternately by a linear system approach (Fig. 2). In this approach, dynamic relations between the solute input on the soil surface and its subsequent downward movement are established in terms of system response functions. This approach incorporates simplified treatments of solute and water flow and makes no claim to fundamentality but does require less input data and computational effort.
The system approach was successfully applied in the unit hydrograph method for the analysis of watershed rainfall-runoff processes (Dooge 1973). A nonlinear watershed response model was later developed based on a truncated Volterra series (Liu and Brutsaert 1978). The system approach has recently been used in modeling solute transport in soils and groundwater bodies (Jury 1982; Duffy and Gelhar 1985; Jury, Sposito, and White 1986; Dyson and White 1987; Liu 1988).

The methodology is to consider a soil column a one-dimensional system. Instead of finding solute concentration distribution in soil directly, we first determine the system's impulse response function, which is the response of the system to a unit impulse input and which embodies a system's inherent characteristics. Then, for any input, the output can be found by the convolution equation, which is an integral expression of the relationship between output, input, and impulse response function.

### LINEAR SYSTEM MODEL OF SOLUTE TRANSPORT IN SOILS

According to the physically based modeling approach, a number of hydrodynamic and reaction kinetics mechanisms may affect, to a varying degree, the solute transport in an unsaturated soil. The intimate dynamic structure of the soil system, which results from the joint effects of all of these mechanisms, is usually only partially understood. However, from a phenomenological viewpoint, we may lump these mechanisms by their attenuation and retardation effects on solute transport, which, in turn, depends on the entire history of a soil system. Mathematically, solute transport can be described as

\[
Q(t) = F \left[ \frac{Q_i(t)}{2} \right], \tag{3}
\]

where \( Q \) is the rate of loss of chemical residual from the soil, \( F \) is a functional of \( Q_i \), and \( Q_i \) is the rate of chemical entry into the soil.
In general, equation (3) can be expressed as a Volterra integral series that consists of linear and nonlinear elements. A truncated second-order Volterra series was used to approximate the nonlinear response of a watershed to rainfall input (Liu and Brutsaert 1978). The application of a higher-order Volterra series model requires the evaluation of a number of response functions, or the kernels of the multiple-integral expansion, which remains a prohibitive task because of mathematical difficulties. Most engineering applications consider only linear systems.

If the soil system is posited to be linear, then the chemical leaving the soil at its lower boundary, Q, relative to the chemical input on the soil surface, Q_i, can be determined by applying the Volterra-type integral equation:

\[ Q(t) = Q_0(t) + \int_{-\infty}^{t} Q_i(\tau) \cdot h(t,\tau) \, d\tau , \tag{4} \]

where Q(t) is the system output or current state of the system, and Q_0(t) the zero-input response of the system or the state of the system without the impact of past inputs. The integral in equation (3) represents the impact of all past inputs Q_i on the current state of the system. The impulse response function h is essentially a weighting factor that transfers the relative importance of past inputs to the current state of the system. Note that the system described by equation (4) is time-invariant if h is only a function of t - \tau, in which case it is also called a convolution equation.

For a solute-soil system without any initial residual chemical and with steady-state flow, equation (4) can be rewritten as follows to evaluate the corresponding chemical flux concentrations:

\[ C(t) = \int_{0}^{t} C_i \cdot h(t-\tau) \, d\tau . \tag{5} \]

In a given system, the impulse response function plays a decisive role. Once it is determined, the characteristics of the system are said to be known. Thus, for any given input C_i, we can calculate C with equation (5).

**SYSTEM IDENTIFICATION TECHNIQUES**

The impulse response function of a linear system model describes the overall effects of the hydrodynamic and reaction mechanisms of a soil-solute system such that specific solute concentration profiles will occur with specific solute inputs. Thus, the success of system modeling depends largely on how accurately and efficiently the impulse response function can be evaluated. The process of finding the system response function is called system identification.
Many techniques have been developed in the identification of the system impulse response function, or linear kernel. Generally, system identification can be accomplished by using one of three methods: (1) system inversion, or black-box method, (2) system parameterization, or grey-box method, or (3) physical parameterization, or white-box method.

In the first method, the impulse response function is determined from given input and output data; no a priori information on the system structure and behavior is assumed. This is why it is also called the black-box model. One example is the unit hydrograph method, for which the impulse response function, or the instantaneous unit hydrograph, is evaluated on the basis of given effective rainfall (input) and direct runoff (output) (Dooge 1973). As the functional series of the Volterra model is essentially a smoothing operation, small errors in input and output data may produce large deviations of the calculated impulse response function (Distefano 1974). To overcome this problem, it is sometimes necessary to introduce system optimization techniques (Liu and Brutsaert 1978) or to conduct frequency-domain analysis (Bras and Rodriguez-Iturbe 1985). Since this method requires rather large amounts of well-structured field data, which are usually unavailable for the problem of solute transport in soil, it will not be discussed in this report.

In the second method, the dynamic nature of solute transport processes is assumed to be partially known, so the impulse response function can be represented by a specific distribution function. Jury (1982) suggested that a log-normal distribution function can be used for many field soils. By so doing, the impulse response function can be derived if two parameters of a specific log-normal distribution (i.e., mean and standard deviation) are calculated. Because of the preferential flow effect and the exchange of concentrations between mobile and immobile waters, the log-normal distribution cannot describe satisfactorily the solute transport in aggregated Hawaiian soils, which show distinct heterogeneous hydrodynamic and dispersive properties. In this study, we found that gamma distribution is more suitable for the purpose.

In physical parameterization, the third method, the impulse response function is expressed as a function of physical parameters that describe hydrodynamic and reaction mechanisms. A physically based model, or convection-dispersion equation, is formulated, then the impulse response function is determined as the model solution with Dirac delta function input.

APPLICATION OF PHYSICAL PARAMETERIZATION METHOD

In this method, the impulse response function is found by using a physically based model. The model consists of mathematical equations that govern the solute transport process in soils. In 1962, Biggar and Nielsen advanced the one-dimensional convection-dispersion transport
model. In this model, solute transport was composed of advection and dispersion. A linear equilibrium sorption between solute and solid was assumed. With simple boundary conditions, the model can be solved analytically. This model is too simple to satisfactorily simulate solute transport in aggregated soils. In 1976, Van Genuchten and Wierenga developed a two-component model, which partitioned soil water into two parts: mobile water and immobile water. Mobile water was in inter-aggregated pores and contributed to solute advection and dispersion. Immobile water was in intra-aggregated pores and would take in solute from or release it to mobile water through a mass transfer process similar to diffusion. This process is called bypassing or preferential flow, which is governed by a first-order kinetic equation. Again, a linear equilibrium sorption reaction between solute and solids was assumed. There are some other models, such as the one-site kinetic adsorption model (Lindstrom 1976) and two-site equilibrium/kinetic sorption model (Nielsen, Van Genuchten, and Biggar 1986; Van Genuchten and Wagenet 1989), neither of which considered immobile water.

The basic idea of the two-component model is that soil water has two phases: mobile and immobile water. Besides the convection-dispersion movement, there is a mass transfer between the two phases, and sorption processes between mobile water and solids and between immobile water and solids are in linear equilibrium. The last condition may not be met, however, in pesticide transport in field soils. After pesticide is applied to the soil surface, it either enters immobile water or adsorbs on the surface of soil particles; the remainder moves forward with mobile water at a lower concentration, to be retained and so on. This lack of equilibrium allows a large amount of pesticide to be retained in topsoil (Davidson, Rieck, and Santelman 1968).

We revised the two-component model and considered a kinetic mass transfer process between mobile water and immobile water. Solids only adsorb solute from immobile water, and the sorption was considered to be in linear equilibrium, with a constant sorption coefficient. Figure 3 shows the modified model. In the figure, \( C_m, C_i, \) and \( C_s \) denote, respectively, the concentration in mobile water, immobile water, and solids. \( C_s \) equals \( C_i \) multiplied by a coefficient \( k_i \).

In this case, the convection-dispersion equation takes the following form:

\[
p \rho \, k_i \frac{\partial C_i}{\partial t} + \theta_m \frac{\partial C_m}{\partial t} + \theta_i \frac{\partial C_i}{\partial t} + V \theta_m \frac{\partial C_m}{\partial z} = D \theta_m \frac{\partial^2 C_m}{\partial z^2}, \tag{6}
\]

where

- \( \rho \) = soil bulk density (\( \mu g/cm^3 \))
- \( k_i \) = sorption coefficient between soil and immobile water (\( cm^3/g \))
- \( C_i \) = solute concentration in mobile water (\( \mu g/cm^3 \))
- \( \theta_m \) = mobile water content (%)
Convection and Dispersion

Mobile Water ($C_m$)

Solids ($C_s$)

Immobile Water ($C_i$)

Figure 3. Revised two-component solute transport model

$C_m =$ solute concentration in mobile water ($\mu$g/cm$^3$)

$\theta_i =$ immobile water content (%)

$V =$ effective water-flow velocity (cm/day)

$Z =$ soil depth (cm)

$D =$ hydrodynamic dispersion coefficient (cm$^2$/day).

We assume that the mass transfer process between mobile and immobile water, including adsorption and desorption, can be controlled by a first-order kinetic. An additional equation can thus be derived, as follows:

$$\frac{\partial C_i}{\partial t} = k_{ad} C_m - k_{de} C_i,$$

Equation (6) describes the convection-dispersion movement in mobile water, which is based on Fick's law and mass balance law. Equation (7) governs the mass transfer between the two water phases. The reason for introducing $k_{ad}$ and $k_{de}$ is that the mass transfer process from mobile water to immobile water (inactivation) is much faster than that from immobile water to mobile water (reactivation). This means that if pesticide is applied, it will be inactivated from mobile water to immobile water and adsorbed by solids quickly, then slowly reactivated when released in mobile water after mobile concentration decreases. Since the release process is very slow, the pesticide will be retained in topsoil for a long time, sometimes more than one year. This agrees with the situation in Hawaiian soils (Schneider and Green 1989). For computational convenience, equations (6) and (7) can be mathematically transformed to the dimensionless form, as follows:
Inverting $B(s)$ back to the time domain, we can obtain the impulse response function $h(t)$. For specific parameters of soil-solute transport, the curve of $h(t)$ will vary accordingly. Normally, it is a single peak curve with positive value and skewness. Figure 4 represents a typical example of $h(t)$.

The impulse response function $h(t)$ is obtained by using numerical Laplace inversion. The convolution equation is solved by numerical integration.

\[ BR \frac{\partial C_i}{\partial T} + \frac{\partial C_m}{\partial T} = \frac{1}{P} \frac{\partial^2 C_m}{\partial X^2} - \frac{\partial C_m}{\partial X} \]  
\[ \text{(8)} \]

and

\[ \frac{\partial C_i}{\partial T} = W_1 C_m - W_2 C_i, \]  
\[ \text{(9)} \]

where $B =$ ratio of immobile water content to mobile water content ($\theta_i/\theta_m$)  
$R =$ retardation factor, which represents the sorption effect [$1 + (p k_i/\theta_i)$]  
$T =$ dimensionless time or pore volume ($V_t/L$)  
$P =$ Paclet number, the ratio of convection to dispersion in the mobile zone ($V_t/D$)  
$X =$ dimensionless soil depth ($Z/L$)  
$W_1 =$ dimensionless inactivate coefficient ($k_{ad} L/V$)  
$W_2 =$ dimensionless reactivate coefficient ($k_{de} L/V$)  
$L =$ characteristic length, which can be a soil depth.

In equation (8), the influence of solid sorption is implied by retardation parameter $R$, which extends immobile water content by converting solid volume into equivalent immobile water content.

The coupled equations (8) and (9) can be solved numerically. But in the system approach, we first find the impulse response function of the system described by these two equations. Given an impulse input, the system transfer function $H(s)$, the analytical solution to equations (8) and (9) in complex domain can be found by Laplace transformation (Liu and Feng 1988). For the revised two-component model, we have

\[ H(s) = \theta_m H_m + R \theta_i H_{im}, \]  
\[ \text{(10)} \]

where

\[ H_m = \exp \left\{ X \left[ \frac{P}{2} - \frac{1}{2} \sqrt{P^2 + 4Ps \left( \frac{BRW_1}{W_2 + s} + 1 \right)} \right] \right\} \]

\[ H_{im} = \frac{W_1 H_m}{W_2 + s}. \]

Inverting $H(s)$ back to the time domain, we can obtain the impulse response function $h(t)$. For specific parameters of soil-solute transport, the curve of $h(t)$ will vary accordingly. Normally, it is a single peak curve with positive value and skewness. Figure 4 represents a typical example of $h(t)$.

The impulse response function $h(t)$ is obtained by using numerical Laplace inversion. The convolution equation is solved by numerical integration.
Owing to the heterogeneity of soil, the column can be divided into several layers, each of which can be assumed to be homogeneous. From a system point of view, each layer is a subsystem and can be analyzed using the same approach, keeping in mind that the output of an upper layer is the input of a lower layer. Therefore, the numerical integrations are expressed as

\[C_m(X_i+1, T_j) = \sum_{k=1}^{n} C_m(X_i, T_j - k\Delta\tau) h_m(X_i, k\Delta\tau) \Delta\tau \] (11)

and

\[C_i(X_i+1, T_j) = \sum_{k=1}^{n} C_m(X_i, T_j - k\Delta\tau) h(X_i, k\Delta\tau) \Delta\tau , \] (12)

where \(h_m\) = inversion of \(H_m\) from complex domain to time domain
\(h\) = inversion of \(H\) from complex domain to time domain
\(i\) = \(i\)th layer of soil column
\(j\) = \(j\)th integral interval of time
\(n\) = \(T_j/\Delta\tau\).

Figure 5 is the sketch of this system modeling approach. The impulse response functions for each layer were obtained through the physically based model described in equations (6) and (7). This implies the two approaches are mathematically equivalent.

Since each layer of soil has different properties, their impulse response functions will be different. The most likely situation is that the impulse response function of the upper layer will be flatter than that of the lower layer because the value of the adsorption coefficient normally drops as soil depth increases. Given \(C_0(t)\), we can derive \(C_1(t)\), \(C_2(t)\), and so on, by using equations (11) and (12) iteratively. When we obtain the concentration distribution with respect
Figure 5. Simulation of solute transport in upper soil by a system modeling approach.

to time for different layers, we can find the concentration distribution with respect to soil depth at different times if the layer is sufficiently narrow.

The white-box model was applied to the data of Fenamiphos experiments conducted at a pineapple field in Kunia, O‘ahu, Hawai‘i. Fenamiphos was applied four times over the field by drip irrigation at a rate of 3.4 kg/ha. Each application lasted three hours. Table 1 is a calendar of the experiment events. During the period without chemical application, the field was subject to both regular water irrigation (14 mm/wk) and irregular rainfall events (1000 ml/yr). Based on the amount of Fenamiphos and water used in one application, the Fenamiphos concentration of the irrigation water was calculated to be 40 mg/l. Part of the soil property data—such as water content, bulk density, and dispersion coefficient—were from laboratory experiments; other data, such as mobile/immobile water content and inactivate/reactivate coefficients, were from model calibration. Table 2 is a list of the basic soil transport parameters. In the simulation, the soil column of 50-cm depth was divided into five 10-cm-thick layers to account for property variation with depth. As a result, five impulse response functions were derived. Table 3 gives the computational results. Figure 6 gives the impulse response functions.
TABLE 1. EXPERIMENT CALENDAR AT KUNIA SITE, O'AHU, HAWAI'I

<table>
<thead>
<tr>
<th>Event</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3-D Fumigation</td>
<td>11/25/86</td>
</tr>
<tr>
<td>Planting</td>
<td>12/05/85</td>
</tr>
<tr>
<td>First Fenamiphos Application</td>
<td>02/27/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>03/23/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>04/20/87</td>
</tr>
<tr>
<td>Second Fenamiphos Application</td>
<td>04/24/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>06/03/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>07/14/87</td>
</tr>
<tr>
<td>Third Fenamiphos Application</td>
<td>07/24/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>09/24/87</td>
</tr>
<tr>
<td>Fourth Fenamiphos Application</td>
<td>11/06/87</td>
</tr>
<tr>
<td>Forcing</td>
<td>11/01/87</td>
</tr>
<tr>
<td>Measurement</td>
<td>01/05/88</td>
</tr>
<tr>
<td>Measurement</td>
<td>03/31/88</td>
</tr>
<tr>
<td>Harvesting</td>
<td>06/88</td>
</tr>
</tbody>
</table>

TABLE 2. BASIC PARAMETERS AT KUNIA SITE, O'AHU, HAWAI'I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Rainfall (mm)</td>
<td>1 000</td>
</tr>
<tr>
<td>Drip Irrigation (mm/wk)</td>
<td>16</td>
</tr>
<tr>
<td>Bulk Density of Soil (g/cm³)</td>
<td>1.05</td>
</tr>
<tr>
<td>Mobile Water Content (%)</td>
<td>15</td>
</tr>
<tr>
<td>Immobile Water Content (%)</td>
<td>15</td>
</tr>
<tr>
<td>Effective Water Velocity (cm/day)</td>
<td>100</td>
</tr>
<tr>
<td>Dispersion Coefficient (cm²/day)</td>
<td>10</td>
</tr>
<tr>
<td>Inactive Coefficient (1/day)</td>
<td>3.0</td>
</tr>
<tr>
<td>Reactivate Coefficient (1/day)</td>
<td>0.03</td>
</tr>
<tr>
<td>Input Concentration of First Layer (mg/l)</td>
<td>40</td>
</tr>
</tbody>
</table>

Figures 7 to 11 show the distribution of Fenamiphos concentration with respect to time. Figure 16 shows the simulated concentration distribution and measured data along the soil depth 396 days after the first application of Fenamiphos.

The shape of curves in Figure 6 suggests that the impulse response functions approximate the form of exponential function. This means that for highly retentive soil, Fenamiphos will be inactivated quickly by immobile water and solids and then reactivated gradually when
<table>
<thead>
<tr>
<th>DEPTH (cm)</th>
<th>0.13</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
<th>3.00</th>
<th>5.00</th>
<th>10.00</th>
<th>13.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.403</td>
<td>0.278</td>
<td>0.278</td>
<td>0.278</td>
<td>0.278</td>
<td>0.277</td>
<td>0.277</td>
<td>0.276</td>
<td>0.272</td>
<td>0.270</td>
</tr>
<tr>
<td>20</td>
<td>0.436</td>
<td>0.259</td>
<td>0.259</td>
<td>0.258</td>
<td>0.258</td>
<td>0.257</td>
<td>0.256</td>
<td>0.253</td>
<td>0.246</td>
<td>0.242</td>
</tr>
<tr>
<td>30</td>
<td>0.457</td>
<td>0.158</td>
<td>0.158</td>
<td>0.157</td>
<td>0.157</td>
<td>0.156</td>
<td>0.156</td>
<td>0.154</td>
<td>0.149</td>
<td>0.146</td>
</tr>
<tr>
<td>40</td>
<td>0.451</td>
<td>0.094</td>
<td>0.093</td>
<td>0.093</td>
<td>0.093</td>
<td>0.092</td>
<td>0.091</td>
<td>0.089</td>
<td>0.088</td>
<td>0.088</td>
</tr>
<tr>
<td>50</td>
<td>0.442</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Parameter Values: \( \text{PB} = 1.05, \text{D} = 10.0, \text{RAFA1} = 3.0, \text{RAFA2} = 0.03, \text{L} = 50.0, \text{V} = 100.0, \text{CITA1} = 0.15, \text{FIM(1)} = 1.00, \text{KD(1)} = 60.0. \)
TABLE 3.2. SIMULATION RESULTS OF FENAMIPHOS TRANSPORT USING REVISED TWO-COMPONENT SOLUTE TRANSPORT MODEL: TOTAL CONCENTRATION IN SOIL

<table>
<thead>
<tr>
<th>DEPTH (cm)</th>
<th>0.13</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
<th>3.00</th>
<th>5.00</th>
<th>10.00</th>
<th>13.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.209</td>
<td>2.782</td>
<td>2.780</td>
<td>2.779</td>
<td>2.776</td>
<td>2.774</td>
<td>2.768</td>
<td>2.757</td>
<td>2.725</td>
<td>2.701</td>
</tr>
<tr>
<td>20</td>
<td>0.981</td>
<td>0.587</td>
<td>0.590</td>
<td>0.597</td>
<td>0.604</td>
<td>0.611</td>
<td>0.624</td>
<td>0.650</td>
<td>0.711</td>
<td>0.745</td>
</tr>
<tr>
<td>30</td>
<td>0.321</td>
<td>0.113</td>
<td>0.114</td>
<td>0.116</td>
<td>0.118</td>
<td>0.120</td>
<td>0.125</td>
<td>0.133</td>
<td>0.154</td>
<td>0.166</td>
</tr>
<tr>
<td>40</td>
<td>0.161</td>
<td>0.034</td>
<td>0.035</td>
<td>0.036</td>
<td>0.036</td>
<td>0.037</td>
<td>0.039</td>
<td>0.041</td>
<td>0.049</td>
<td>0.053</td>
</tr>
<tr>
<td>50</td>
<td>0.095</td>
<td>0.008</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td>0.010</td>
<td>0.012</td>
<td>0.013</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TIME (day)</th>
<th>15.0</th>
<th>17.0</th>
<th>20.0</th>
<th>24.0</th>
<th>30.0</th>
<th>35.0</th>
<th>40.0</th>
<th>45.0</th>
<th>52.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.685</td>
<td>2.667</td>
<td>2.639</td>
<td>2.599</td>
<td>2.533</td>
<td>2.475</td>
<td>2.413</td>
<td>2.349</td>
<td>2.257</td>
</tr>
<tr>
<td>20</td>
<td>0.766</td>
<td>0.786</td>
<td>0.815</td>
<td>0.851</td>
<td>0.898</td>
<td>0.932</td>
<td>0.961</td>
<td>0.986</td>
<td>1.014</td>
</tr>
<tr>
<td>30</td>
<td>0.174</td>
<td>0.182</td>
<td>0.193</td>
<td>0.208</td>
<td>0.229</td>
<td>0.246</td>
<td>0.262</td>
<td>0.277</td>
<td>0.296</td>
</tr>
<tr>
<td>40</td>
<td>0.056</td>
<td>0.059</td>
<td>0.063</td>
<td>0.069</td>
<td>0.077</td>
<td>0.083</td>
<td>0.090</td>
<td>0.096</td>
<td>0.104</td>
</tr>
<tr>
<td>50</td>
<td>0.014</td>
<td>0.015</td>
<td>0.016</td>
<td>0.017</td>
<td>0.020</td>
<td>0.022</td>
<td>0.023</td>
<td>0.025</td>
<td>0.028</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10</th>
<th>56.13</th>
<th>56.25</th>
<th>60.0</th>
<th>65.0</th>
<th>70.0</th>
<th>80.0</th>
<th>96.0</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.320</td>
<td>0.303</td>
<td>0.281</td>
<td>0.281</td>
<td>0.281</td>
<td>0.281</td>
<td>0.281</td>
<td>0.281</td>
<td>0.281</td>
</tr>
<tr>
<td>30</td>
<td>0.756</td>
<td>0.770</td>
<td>0.787</td>
<td>1.108</td>
<td>0.900</td>
<td>0.916</td>
<td>0.967</td>
<td>1.011</td>
<td>1.048</td>
</tr>
<tr>
<td>40</td>
<td>0.297</td>
<td>0.307</td>
<td>0.320</td>
<td>0.481</td>
<td>0.354</td>
<td>0.362</td>
<td>0.387</td>
<td>0.410</td>
<td>0.430</td>
</tr>
<tr>
<td>50</td>
<td>0.086</td>
<td>0.089</td>
<td>0.094</td>
<td>0.190</td>
<td>0.103</td>
<td>0.105</td>
<td>0.114</td>
<td>0.122</td>
<td>0.136</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10</th>
<th>205</th>
<th>210</th>
<th>220</th>
<th>230</th>
<th>249</th>
<th>249.13</th>
<th>249.25</th>
<th>250</th>
<th>260</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.839</td>
<td>3.693</td>
<td>3.408</td>
<td>3.136</td>
<td>2.657</td>
<td>2.682</td>
<td>5.433</td>
<td>5.412</td>
<td>5.121</td>
</tr>
<tr>
<td>30</td>
<td>2.639</td>
<td>2.613</td>
<td>2.551</td>
<td>2.477</td>
<td>2.316</td>
<td>2.395</td>
<td>2.900</td>
<td>2.904</td>
<td>2.935</td>
</tr>
<tr>
<td>40</td>
<td>1.110</td>
<td>1.117</td>
<td>1.127</td>
<td>1.132</td>
<td>1.128</td>
<td>1.148</td>
<td>1.241</td>
<td>1.243</td>
<td>1.276</td>
</tr>
<tr>
<td>50</td>
<td>0.473</td>
<td>0.480</td>
<td>0.492</td>
<td>0.502</td>
<td>0.516</td>
<td>0.678</td>
<td>0.551</td>
<td>0.552</td>
<td>0.571</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10</th>
<th>280</th>
<th>290</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>330</th>
<th>340</th>
<th>350</th>
<th>360</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.920</td>
<td>2.881</td>
<td>2.824</td>
<td>2.754</td>
<td>2.673</td>
<td>2.583</td>
<td>2.486</td>
<td>2.383</td>
<td>2.278</td>
</tr>
<tr>
<td>40</td>
<td>1.321</td>
<td>1.333</td>
<td>1.340</td>
<td>1.341</td>
<td>1.337</td>
<td>1.328</td>
<td>1.315</td>
<td>1.298</td>
<td>1.277</td>
</tr>
<tr>
<td>50</td>
<td>0.603</td>
<td>0.616</td>
<td>0.626</td>
<td>0.635</td>
<td>0.641</td>
<td>0.646</td>
<td>0.648</td>
<td>0.649</td>
<td>0.648</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10</th>
<th>380</th>
<th>396</th>
<th>410</th>
<th>420</th>
<th>430</th>
<th>440</th>
<th>450</th>
<th>460</th>
<th>470</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.947</td>
<td>1.665</td>
<td>1.448</td>
<td>1.308</td>
<td>1.179</td>
<td>1.062</td>
<td>0.956</td>
<td>0.858</td>
<td>0.770</td>
</tr>
<tr>
<td>30</td>
<td>1.262</td>
<td>1.189</td>
<td>1.171</td>
<td>1.138</td>
<td>1.137</td>
<td>1.138</td>
<td>1.134</td>
<td>1.148</td>
<td>1.174</td>
</tr>
<tr>
<td>40</td>
<td>0.642</td>
<td>0.633</td>
<td>0.623</td>
<td>0.614</td>
<td>0.605</td>
<td>0.594</td>
<td>0.583</td>
<td>0.572</td>
<td>0.560</td>
</tr>
<tr>
<td>50</td>
<td>0.240</td>
<td>0.242</td>
<td>0.243</td>
<td>0.243</td>
<td>0.243</td>
<td>0.243</td>
<td>0.243</td>
<td>0.241</td>
<td>0.240</td>
</tr>
</tbody>
</table>

Parameter Values: PB = 1.05, D = 10.0, RAFA1 = 3.0, RAFA2 = 0.03, L = 50.0, V = 100.0, CTAA(1) = 0.15, FIIM(1) = 1.00, KD(1) = 0.60.
<table>
<thead>
<tr>
<th>DEPTH (cm)</th>
<th>0.13</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
<th>3.00</th>
<th>5.00</th>
<th>10.00</th>
<th>13.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>10</td>
<td>9.006</td>
<td>.033</td>
<td>.033</td>
<td>.032</td>
<td>.032</td>
<td>.032</td>
<td>.032</td>
<td>.032</td>
<td>.031</td>
<td>.030</td>
</tr>
<tr>
<td>30</td>
<td>1.431</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
</tr>
<tr>
<td>40</td>
<td>.864</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
<td>.006</td>
<td>.006</td>
</tr>
<tr>
<td>50</td>
<td>.586</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
</tr>
<tr>
<td>0</td>
<td>0.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>10</td>
<td>.028</td>
<td>.028</td>
<td>.027</td>
<td>.026</td>
<td>.024</td>
<td>.023</td>
<td>.022</td>
<td>.021</td>
<td>.019</td>
<td>.019</td>
</tr>
<tr>
<td>20</td>
<td>.016</td>
<td>.016</td>
<td>.016</td>
<td>.016</td>
<td>.015</td>
<td>.015</td>
<td>.015</td>
<td>.015</td>
<td>.015</td>
<td>.014</td>
</tr>
<tr>
<td>30</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
</tr>
<tr>
<td>50</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
<td>.004</td>
</tr>
<tr>
<td>0</td>
<td>56.13</td>
<td>56.25</td>
<td>60.0</td>
<td>65.0</td>
<td>70.0</td>
<td>80.0</td>
<td>96.0</td>
<td>100</td>
<td>110</td>
<td>120</td>
</tr>
<tr>
<td>10</td>
<td>40.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>20</td>
<td>2.819</td>
<td>.030</td>
<td>.030</td>
<td>.030</td>
<td>.029</td>
<td>.027</td>
<td>.027</td>
<td>.026</td>
<td>.026</td>
<td>.024</td>
</tr>
<tr>
<td>30</td>
<td>1.440</td>
<td>.018</td>
<td>.018</td>
<td>.018</td>
<td>.018</td>
<td>.017</td>
<td>.017</td>
<td>.017</td>
<td>.017</td>
<td>.017</td>
</tr>
<tr>
<td>50</td>
<td>.590</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
</tr>
<tr>
<td>0</td>
<td>130</td>
<td>137</td>
<td>147</td>
<td>147.13</td>
<td>147.25</td>
<td>150</td>
<td>160</td>
<td>170</td>
<td>180</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>.024</td>
<td>.022</td>
<td>.019</td>
<td>9.025</td>
<td>.052</td>
<td>.051</td>
<td>.046</td>
<td>.041</td>
<td>.037</td>
<td>.033</td>
</tr>
<tr>
<td>20</td>
<td>.023</td>
<td>.022</td>
<td>.021</td>
<td>2.826</td>
<td>.037</td>
<td>.037</td>
<td>.035</td>
<td>.034</td>
<td>.033</td>
<td>.031</td>
</tr>
<tr>
<td>30</td>
<td>.016</td>
<td>.016</td>
<td>.015</td>
<td>1.446</td>
<td>.024</td>
<td>.024</td>
<td>.023</td>
<td>.023</td>
<td>.022</td>
<td>.022</td>
</tr>
<tr>
<td>40</td>
<td>.011</td>
<td>.011</td>
<td>.010</td>
<td>.874</td>
<td>.016</td>
<td>.016</td>
<td>.016</td>
<td>.015</td>
<td>.015</td>
<td>.015</td>
</tr>
<tr>
<td>50</td>
<td>.008</td>
<td>.007</td>
<td>.007</td>
<td>.593</td>
<td>.011</td>
<td>.011</td>
<td>.011</td>
<td>.011</td>
<td>.011</td>
<td>.010</td>
</tr>
<tr>
<td>0</td>
<td>205</td>
<td>210</td>
<td>220</td>
<td>230</td>
<td>249</td>
<td>249.13</td>
<td>249.25</td>
<td>250</td>
<td>260</td>
<td>270</td>
</tr>
<tr>
<td>10</td>
<td>.028</td>
<td>.027</td>
<td>.024</td>
<td>.021</td>
<td>.017</td>
<td>9.023</td>
<td>.050</td>
<td>.049</td>
<td>.045</td>
<td>.040</td>
</tr>
<tr>
<td>20</td>
<td>.029</td>
<td>.028</td>
<td>.026</td>
<td>.025</td>
<td>.022</td>
<td>2.826</td>
<td>.038</td>
<td>.038</td>
<td>.036</td>
<td>.035</td>
</tr>
<tr>
<td>30</td>
<td>.021</td>
<td>.020</td>
<td>.020</td>
<td>.019</td>
<td>.017</td>
<td>1.448</td>
<td>.026</td>
<td>.026</td>
<td>.025</td>
<td>.025</td>
</tr>
<tr>
<td>40</td>
<td>.014</td>
<td>.014</td>
<td>.014</td>
<td>.013</td>
<td>.012</td>
<td>.876</td>
<td>.018</td>
<td>.018</td>
<td>.018</td>
<td>.017</td>
</tr>
<tr>
<td>50</td>
<td>.010</td>
<td>.010</td>
<td>.010</td>
<td>.009</td>
<td>.009</td>
<td>.595</td>
<td>.012</td>
<td>.012</td>
<td>.012</td>
<td>.012</td>
</tr>
<tr>
<td>0</td>
<td>280</td>
<td>290</td>
<td>300</td>
<td>310</td>
<td>320</td>
<td>330</td>
<td>340</td>
<td>350</td>
<td>360</td>
<td>370</td>
</tr>
<tr>
<td>10</td>
<td>.036</td>
<td>.032</td>
<td>.029</td>
<td>.026</td>
<td>.023</td>
<td>.021</td>
<td>.019</td>
<td>.016</td>
<td>.015</td>
<td>.013</td>
</tr>
<tr>
<td>20</td>
<td>.033</td>
<td>.031</td>
<td>.030</td>
<td>.028</td>
<td>.026</td>
<td>.025</td>
<td>.023</td>
<td>.022</td>
<td>.020</td>
<td>.019</td>
</tr>
<tr>
<td>30</td>
<td>.024</td>
<td>.023</td>
<td>.022</td>
<td>.022</td>
<td>.021</td>
<td>.020</td>
<td>.019</td>
<td>.018</td>
<td>.017</td>
<td>.016</td>
</tr>
<tr>
<td>40</td>
<td>.017</td>
<td>.016</td>
<td>.016</td>
<td>.015</td>
<td>.015</td>
<td>.014</td>
<td>.014</td>
<td>.013</td>
<td>.013</td>
<td>.012</td>
</tr>
<tr>
<td>50</td>
<td>.012</td>
<td>.012</td>
<td>.011</td>
<td>.011</td>
<td>.011</td>
<td>.010</td>
<td>.010</td>
<td>.009</td>
<td>.009</td>
<td>.009</td>
</tr>
<tr>
<td>0</td>
<td>380</td>
<td>396</td>
<td>410</td>
<td>420</td>
<td>430</td>
<td>440</td>
<td>450</td>
<td>460</td>
<td>470</td>
<td>480</td>
</tr>
<tr>
<td>10</td>
<td>.012</td>
<td>.010</td>
<td>.008</td>
<td>.007</td>
<td>.006</td>
<td>.006</td>
<td>.005</td>
<td>.004</td>
<td>.004</td>
<td>.003</td>
</tr>
<tr>
<td>20</td>
<td>.017</td>
<td>.015</td>
<td>.014</td>
<td>.013</td>
<td>.012</td>
<td>.011</td>
<td>.010</td>
<td>.009</td>
<td>.008</td>
<td>.008</td>
</tr>
<tr>
<td>30</td>
<td>.015</td>
<td>.014</td>
<td>.013</td>
<td>.012</td>
<td>.011</td>
<td>.011</td>
<td>.010</td>
<td>.009</td>
<td>.009</td>
<td>.008</td>
</tr>
<tr>
<td>40</td>
<td>.012</td>
<td>.011</td>
<td>.010</td>
<td>.010</td>
<td>.009</td>
<td>.009</td>
<td>.008</td>
<td>.008</td>
<td>.007</td>
<td>.007</td>
</tr>
<tr>
<td>50</td>
<td>.008</td>
<td>.008</td>
<td>.007</td>
<td>.007</td>
<td>.007</td>
<td>.006</td>
<td>.006</td>
<td>.006</td>
<td>.006</td>
<td>.005</td>
</tr>
</tbody>
</table>

Parameter Values: $PB = 1.05$, $D = 10.0$, $RAFA1 = 3.0$, $RAFA2 = 0.03$, $L = 50.0$, $V = 100.0$, $CITA(1) = 0.15$, $FIM(1) = 1.00$, $KD(1) = 0.60$. 
Figure 6. Impulse response functions of five soil-solute systems

Figure 7. Fenamiphos concentration distribution in soil at 10-cm depth, Kunia site, O'ahu, Hawai'i
Figure 8. Fenamiphos concentration distribution in soil at 20-cm depth, Kunia site, O'ahu, Hawai'i

Figure 9. Fenamiphos concentration distribution in soil at 30-cm depth, Kunia site, O'ahu, Hawai'i
Figure 10. Fenamiphos concentration distribution in soil at 40-cm depth, Kunia site, O'ahu, Hawai'i

Figure 11. Fenamiphos concentration distribution in soil at 50-cm depth, Kunia site, O'ahu, Hawai'i
reentering mobile water. From model calibration, a ratio of inactivate rate to reactivate rate of around 100 is calculated. Because of this high ratio, Fenamiphos was inactivated quickly by the topsoil when it was applied, remaining in intra-aggregate pores; it was then reactivated slowly into inter-aggregate pores when mobile solute concentration became less than that of the immobile solution. This is a reasonable explanation of the phenomenon that Fenamiphos was held in the upper soil more than one year.

Figures 7 to 11 show that at longer periods, the simulation results are closer to the measured data than at shorter periods. This suggests that the physically based two-component transport model may be suitable for describing long-term transport. This is because after a long period, the effect of parameter fluctuation is greatly attenuated by the retardation of soil formation; hence, the average values of the parameters can describe the transport well. Figure 12 illustrates this situation at 396 days.

In a previous study, a similar approach was used by Liu and Feng to simulate DBCP transport at the Kunia site (Liu and Feng 1988). In that study, the impulse response function was not explicitly found but was implicitly used in computer programs. According to our experience, there are, in a certain range, some stability problems caused by numerical truncation in using the International Mathematical and Statistical Library (IMSL) inverse Laplace procedure to find the impulse response function. Such a problem can be avoided with the implicit use of the impulse response function.

In our white-box modeling, the impulse response function of the soil-solute transport system was used either implicitly or explicitly in a physically based model, which in turn is derived by combining bypassing and sorption processes. The results obtained for either case were satisfactory.

APPLICATION OF SYSTEM PARAMETERIZATION METHOD

As mentioned above, system parameterization is also called the grey-box method. Unlike in white-box modeling, we do not assume that all the mechanisms are known, but we do have some information about the system, such as partial knowledge of its internal structure and some input and output data. Utilizing this information, we can find the system impulse response function. The assumption we make here is that the system is linear. The generalized impulse response function has the nature of the probability density function (travel time probability density function, as termed by Sposito et al. 1986), which lumps the net effect of such soil processes as convection, dispersion, sorption, radioactive decay, and biological transformation. A certain type of probability density function is suitable for a certain situation.
The parameters of the distribution are obtained by fitting the experimental data of system input and output to a theoretical distribution.

Solute transport in soil is the combination of many simultaneous processes. Besides convection, dispersion, and degradation, solute may also be retained by soil voids when it enters dead-end pores and intra-pores—both of which form the immobile zone—and may be adsorbed on the surfaces of soil particles by organic matter. The retained solute will then be released gradually into macropores (the mobile zone) when the solute concentration in the mobile zone becomes lower. In unsaturated soil, solute will be retained significantly in the immobile zone due to the suction potential of soil.

These dead-end pores and intra-pores can be considered microreservoirs, while the soil column can be thought of as a cascade of n reservoirs in a series, each having a linear retention-release relation with constant $T$, the delay time of the reservoir. For a given solute input into the first reservoir, the output will be the input into the second reservoir; the output of the second reservoir becomes the input into the third one; and so on. For each reservoir, its linear retention rate equals inflow rate minus outflow rate. This can be written as follows:

$$ T \frac{dC_i}{dt} = C_{i-1} - C_i \quad i = 1,2,\ldots,n $$

(13)
Solving these \( n \) simultaneous equations, we obtain the output of the \( n \)th reservoir:

\[
C_n = \frac{C_0}{T(n-1)!} \left( \frac{1}{T} \right)^{(n-1)} e^{-\left(\frac{t}{T}\right)},
\]

where \( C_0 \) is the input of the first reservoir. If \( C_0 \) is a unit delta pulse, \( C_n \) becomes the impulse response function of this \( n \)-series reservoir system. Obviously, the above expression is a gamma distribution, with \( n \) and \( k \) \((k = 1/T)\) being shape and scale parameters, respectively. This expression is obtained by assuming that each reservoir has a linear retention-release relation, which is the consequence of the assumption that instantaneous complete mixing occurs when a solute enters soil pores. Since the soil pores are not uniform in size and shape, microreservoirs have different delay times. Hence, we use an average delay time \( T \), which can be found by curve fitting.

The mechanical properties of a soil are primarily determined by its particle-size distribution. According to the fractal theory, \( k \) cubes of \( L^3 \) size have a probability of \( p \) to fragment into \( n \) smaller uniform cubes, and a probability of \( (1-p) \) not to fragment. Hence, the number of fragmentations is \( kp \), and the number of nonfragmentations is \( k(1-p) \). Subsequently, \( kp \) fragments into \( kp^2 \) while \( kp(1-p) \) remains unfragmented; and \( k(1-p) \), which does not fragment in the first-stage fragmentation, then fragments into \( k(1-p)p \) while \( k(1-p)^2 \) remains unfragmented. And further fragmentation follows the same rule. Grouping particles of the same size and counting their numbers, we find that particle distribution is a binomial one with the following form:

\[
f(x;n,p) = \binom{n}{x} p^x (1-p)^{n-x} \quad x = 0,1,2,...,n, \tag{15}
\]

where \( x = \) particle-size level.

When \( n \) approaches infinity, binomial distribution becomes Poisson distribution:

\[
f(x;\lambda) = \frac{\lambda^x e^{-\lambda}}{x!} \quad x = 0,1,2,...; \quad \lambda > 0, \tag{16}
\]

where \( \lambda = np \), which is the mean value of the Poisson distribution. It should be noted that if \( \lambda \) is a variable and \( x \) is fixed, a gamma distribution can be derived.

If the soil particle size is of Poisson distribution, we can assume the aggregate size is also of Poisson distribution if the probability of aggregation of primary particles is of uniform distribution. Consequently, the hydraulic conductivity and flow velocity are also of Poisson distribution. The arrival time of solute particles to a fixed spatial point \( x \) will then follow a gamma distribution, which is proved below.
Let \( f(x) \, dx \) be the probability of solute particles travelling between \( x \) and \( x + dx \) at time \( t \), and \( g(t) \, dt \) be the probability that solute particles arrive at \( x \) between \( t \) and \( t + dt \). If \( \lambda = kt \) and \( x = vt \), we have

\[
f(x) = \frac{(kt)^x e^{-kt}}{x!}
\]

and

\[
f(x) \, dx = g(t) \, dt.
\]

Hence,

\[
g(t) = f(x) \frac{dx}{dt}
\]

\[
= \frac{tk^x t^{x-1} e^{-kt}}{x(x-1)!} \cdot v
\]

\[
= \frac{(kt)^x t^{x-1} e^{-kt}}{(x-1)!}.
\]

Therefore, \( g(t) \) is a gamma distribution. Both \( k \) and \( v \) are constants: \( k \) is the mean value of Poisson distribution in a unit time interval; and \( v \) is the flow velocity. The property of \( \lambda = kt \) is known as stationarity, while the property of \( f(x) \, dx = g(t) \, dt \) is known as ergodicity. Furthermore, it is reasonable to postulate that solute concentration distribution in aggregated soils is a gamma distribution with respect to time since solute concentration should be proportional to solute particle number in a unit spatial volume.

After considering linear theory analysis, linear reservoir assumptions, and statistical and fractal theory, we arrived at the conclusion that gamma distribution is an approximate expression of the impulse response function of the soil transport system.

A general form of gamma distribution used in the grey-box model is expressed as follows:

\[
h(t) = C \frac{b^{a+1} e^{-bt} t^a}{\Gamma(a+1)}
\]

\( t \geq 0, \, a \geq 0, \, b \geq 0 \),

where \( a \) is the shape parameter, and \( b \) and \( c \) the scale parameters.

Physically, \( C \) represents the total solute mass applied, \( a \) the depth of the soil column, and \( b \) soil properties such as adsorption ability, water content, and flow velocity. However, the exact relationship among these properties is not known.

A similar approach, called the transfer function model, was proposed by Jury (1982) and essentially bears the same mathematical structure as the grey-box model. However, the assumptions made by Jury were different:

1. Water flow is pistonlike
2. There is no dispersion
3. There is a travel time density function for solute to move from the soil surface to any given depth.

In his model, Jury (1982) used a log-normal distribution as the travel time density function because he found that the water velocity in soil is not uniform but has a log-normal distribution. He only considered advection of the solute while neglecting other mechanisms. Although his model was quite successful in simulating conservative solute transport, it is questionable to extend the log-normal distribution to soils with dispersion, sorption, and other degradation mechanisms. In our study, we found that the gamma distribution is more suitable to the well-structured and aggregated Hawaiian soils.

The equations

\[ C(t) = \int_0^t C_0 (t - \tau) h(\tau) \, d\tau \]  

and

\[ h(t) = \frac{b^{a+1} e^{-bt}}{\Gamma(a + 1)} \]  

are the mathematical expressions for our grey-box model. \( C(t) \) is the output of the system, the solute concentration distribution at the exit of the soil column; \( C_0(t) \) the system input, the solute concentration distribution at the soil-column entrance; and \( h(t) \) the impulse response function of the system having the form of the gamma distribution.

According to the system theory, if a pulse of solute is applied, say \( C_0(t) = m_0 \delta(t) \), the output \( C(t) \) in equation (5) will be \( m_0 h(t) \), where \( m_0 \) is the solute mass constant. Parameters of \( h(t) \), which assumes the form of a gamma distribution, can be found by fitting \( m_0 h(t) \) to measured data \( C(t) \).

By means of mathematical transformation, gamma distribution can be linearized and the parameters can be estimated by the least-square method. The linearization of gamma distribution is based on the following equation:

\[ y = L x^a e^{-bx}, \]  

where \( L \), \( a \), and \( b \) are unknowns and need to be found. Let \( y_i = y_{i-1} + \Delta y \), \( x_i = x_{i-1} + \Delta x \), and \( i = 1, 2, ..., n \). Here, \( n \) is the number of the data points. We can thus derive

\[ \frac{y_i}{y_{i-1}} = \frac{L(x_i + \Delta x)^a e^{-b(x_i + \Delta x)}}{L x_i^a e^{-bx_i}} \]

\[ = \frac{(x_i + \Delta x)^a}{x_i^a} e^{-b\Delta x}. \]  

Let \( Y = \ln(y_i) - \ln(y_{i-1}) \), \( X_1 = \ln(x_i) - \ln(x_{i-1}) \), and \( X_2 = \Delta x \) and the above equation becomes
In summary, our gamma-distribution-type grey-box model is described by equations (21) and (22), and the parameters are estimated by equations (26), (27), and (28). This model was applied to the simulation of the same data on Fenamiphos transport as mentioned in the section on the white-box model. The field data on the distribution of Fenamiphos concentration were fitted to the theoretical gamma distribution to estimate the parameters.

The experimental conditions at the Kunia site were as stated previously. Since the duration of the irrigation was much shorter than the period of the observation, the solute deposited on the surface by means of drip irrigation can be considered an impulse input. Because of the heterogeneity of the soil column, five layers—at the depths of 10 cm, 20 cm, 30 cm, 40 cm, and 50 cm—were used in the simulation, and each was considered a smaller system. The parameters of the gamma distribution model for each of the systems were found by fitting the following equation to the corresponding field data:

\[
Y = aX_1 - bX_2. \tag{25}
\]

Using the least-square method, we obtain

\[
a = \frac{\sum YX_1 - \sum X_2^2 - \sum YX_2 - \sum X_1X_2}{\sum X_2^2 \cdot (\sum X_1)^2 - (\sum X_1X_2)^2}, \tag{26}
\]

\[
b = \frac{a \sum X_1^2 - \sum YX_1}{\sum X_1X_2}, \tag{27}
\]

and

\[
L = \frac{1}{n} \sum_{i=1}^{n} \frac{y_i}{x_i^a e^{bx_i}}. \tag{28}
\]

Table 4 and Figures 13 to 16 present the results of the simulation. Figures 17 to 19 illustrate the relationship between the parameters of the five gamma distribution models and the corresponding soil depths.
TABLE 4. FENAMIPHOS CONCENTRATION DISTRIBUTION

<table>
<thead>
<tr>
<th>SOIL DEPTH (cm)</th>
<th>CONCENTRATION (ppm)</th>
<th>24 days</th>
<th>96 days</th>
<th>205 days</th>
<th>396 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10</td>
<td></td>
<td>2.55</td>
<td>2.99</td>
<td>2.22</td>
<td>0.576</td>
</tr>
<tr>
<td></td>
<td>(3.34)</td>
<td>(2.23)</td>
<td>(1.97)</td>
<td>(2.26)</td>
<td></td>
</tr>
<tr>
<td>10-20</td>
<td></td>
<td>1.81</td>
<td>2.32</td>
<td>1.86</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>(4.05)</td>
<td>(2.45)</td>
<td>(1.87)</td>
<td>(2.26)</td>
<td></td>
</tr>
<tr>
<td>20-30</td>
<td></td>
<td>1.43</td>
<td>2.09</td>
<td>1.90</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>(2.35)</td>
<td>(2.69)</td>
<td>(1.75)</td>
<td>(0.95)</td>
<td></td>
</tr>
<tr>
<td>30-40</td>
<td></td>
<td>0.75</td>
<td>1.26</td>
<td>1.34</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>(1.90)</td>
<td>(1.05)</td>
<td>(1.12)</td>
<td>(0.95)</td>
<td></td>
</tr>
<tr>
<td>40-50</td>
<td></td>
<td>0.274</td>
<td>0.53</td>
<td>0.68</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>(0.52)</td>
<td>(1.05)</td>
<td>(1.12)</td>
<td>(0.21)</td>
<td></td>
</tr>
</tbody>
</table>

Note: Numbers in parentheses are measured data.

Figure 13. Fenamiphos concentration distribution in soil at 24 days, Kunia site, O'ahu, Hawai'i
Figure 14. Fenamiphos concentration distribution in soil at 96 days, Kunia site, O'ahu, Hawai'i

Figure 15. Fenamiphos concentration distribution in soil at 205 days, Kunia site, O'ahu, Hawai'i
Figure 16. Fenamiphos concentration distribution in soil as measured and computed by a grey-box model at 396 days, Kunia site, O'ahu, Hawai'i.

Figure 17. Gamma distribution parameter $a$ and soil depth

$$y = 2.7000 \times 10^{-2} + 2.5000 \times 10^{-3}x$$

$R^2 = 0.995$
\[ y = 1.8200 \times 10^{-2} - 2.8000 \times 10^{-4}x \]
\[ R^2 = 0.995 \]

**Figure 18.** Gamma distribution parameter \( b \) and soil depth

\[ y = 285.00 - 3.5000x \]
\[ R^2 = 0.942 \]

**Figure 19.** System output mass \( M \) and soil depth
Compared with the field data, Figures 13 to 16 show rather satisfactory simulation results, which get better as time passes or soil depth increases. This probably indicates that the gamma distribution model better simulates solute transport at greater distances and over longer periods. This can be explained by the fact that the more solute is retained in small soil pores and does not move down with mobile water, the better the conditions are satisfied under which the gamma distribution is used to approximate the impulse response function of the solute-soil transport system. Figure 17 shows that parameter a increases with depth, which means it is controlled by the soil-pore volume. Figure 18 shows the decrease in parameter b with depth, which suggests that it is controlled by the adsorption process, which diminishes as organic matter decreases with depth. Figure 19 shows the decrease of output mass M with depth, which is expected because the gamma distribution model considers irreversible solute lateral movement, such as decay and immobilization (Selim, Amacher, and Iskandar 1989). These linear relationships provide an insight into and a possible prediction of the distribution of Fenamiphos concentration in the deeper soil zone, for which no field data are available.

CONJUNCTIVE USE OF GREY-BOX AND WHITE-BOX METHODS

Every model has its assumptions and limitations. Physically based models are based on the concept of embedded mechanisms of water—such as convection, or mass flow—and the chemical process of diffusion in response to concentration gradient. All the quantities, parameters, or coefficients used to measure these complex mechanisms need to be determined beforehand. Unfortunately, these coefficients are normally determined in laboratories and, in many cases, have failed to describe the field-scale phenomena due to the scale effect and soil heterogeneity.

System-based models are based on system response functions, which may be associated with the physical mechanisms, i.e., the grey-box method. In the white-box model, the parameters in the response function in the frequency domain are essentially the same as those in the physically based two-component model. The mathematical equivalence of the two is obvious. In the grey-box model, the parameters lump the effects of all the processes together, so the physical meaning of the parameters is difficult to see. Compared to the two-component model, the structure of the grey-box model is simpler, and hence requires fewer input data, no matter what form of probability density function the impulse response function may take, such as the log-normal or gamma distribution form. For managerial purposes, the grey-box model may be more practical and useful.
An interesting aspect of modeling solute transport in the field is the so-called conjunctive use of the physically based model and system-based model, as advanced by Liu (1988). Through conjunctive use of these physically based and system models, we can compare the performance of the two modeling approaches and give additional meaning to the parameters used in a physically based model. For instance, through conjunctive use of the two models, Liu was able to show the compatibility of the two approaches and to prove the length dependence of the dispersion coefficient for a conservative solute transport in heterogeneous soils (Liu 1988).

Since the white-box model used here for the Kunia data is identical with the physically based model, we can deem it another expression of the latter. Hence, we only need to compare the behavior of the white-box and the grey-box models for conjunctive use.

The way to compare the behavior of the two models is to compare their moments (Jury, Sposito, and White 1986; Liu 1988). By so doing, we will be able to find the correlation between the parameters of the gamma distribution and the parameters of the soil-solute transport system.

The moment-generating function of a random variable $t$, which has a probability density distribution $f(t)$, is defined as (Beyer 1978),

$$m_k(z) = E(e^{zt}) = \int_{-\infty}^{\infty} e^{zt} f(t) \, dt,$$

where $E(e^{zt})$ is the expected value of $e^{zt}$, and $z$ is an arbitrary variable in the complex domain:

$$E(e^{zt}) = E \left[ 1 + zt + \frac{(zt)^2}{2!} + \frac{(zt)^3}{3!} + \cdots \right]$$

$$= E(1) + E(t) z + E(t^2) \frac{z^2}{2!} + E(t^3) \frac{z^3}{3!} + \cdots$$

$$= 1 + \mu_1 z + \frac{\mu_2 z^2}{2!} + \frac{\mu_3 z^3}{3!} + \cdots,$$

where $\mu_i$ equals $E(t^i)$ and is the $i$th moment of $t$, which has a distribution $f(t)$ about the origin. Therefore, we have

$$\mu_i = \left[ \frac{d^i m(z)}{dz^i} \right]_{z=0} \quad i = 0,1,2,3,\ldots .$$

The moments thus generated can be related to the Laplace transformation by substituting $z$ with $-s$ and using positive $t$. The $i$th moment of $f(t)$ about the origin will have an $i$th derivative relation with $F(s)$, which is the Laplace transformation of $f(t)$:

$$\mu_i = (-1)^i \left[ \frac{d^i F(s)}{ds^i} \right]_{s=0} \quad i = 0,1,2,3,\ldots .$$
The impulse response function is actually a weighting function and can be interpreted as a probability density function of travel time. Hence, for a linear system, the impulse response function \( h(t) \) has an \( i \)th moment identical to equation (33):

\[
\mu_i = (-1)^i \left[ \frac{d^i H(s)}{ds^i} \right]_{s=0} \quad i = 0,1,2,3,\ldots ,
\]

(34)

where \( H(s) \) is the Laplace transformation of \( h(t) \).

As a direct derivation, the statistical mean \( \mu \), variance \( \sigma^2 \), and skewness \( \gamma \) of distribution \( h(t) \) are, respectively,

\[
\mu = E(t) = \mu_1,
\]

(35)

\[
\sigma^2 = E[(t - \mu)^2] = \mu_2 - \mu^2,
\]

(36)

and

\[
\gamma = E[(t - \mu)^3] = \mu_3 + 3\mu^2 - 3\mu_2 \mu.
\]

(37)

As stated previously in the discussion of equation (10), the revised two-component model has the following Laplace transformation of the impulse response functions for the mobile and immobile components:

\[
H_m(s) = \exp \left\{ X \left[ \frac{P}{2} - \frac{1}{2} \sqrt{P^2 + 4Ps \left( \frac{BRW_1}{W_2 + s} + 1 \right)} \right] \right\}
\]

(38)

and

\[
H_{im}(s) = \frac{W_1 H_m}{W_2 + s}.
\]

(39)

By using equations (34) through (38), the mean \( \mu_m \), variance \( \sigma^2_m \), and skewness \( \gamma_m \) of \( h_m(t) \), the impulse response function of the immobile water component, were found, as follows:

\[
\mu_m = X (1 + \frac{BRW_1}{W_2}),
\]

(40)

\[
\sigma^2_m = X^2 (1 + \frac{BRW_1}{W_2})^2 + \frac{2BRW_1X}{W_2} + \frac{2X}{P} (1 + \frac{BRW_1}{W_2})^2,
\]

(41)

and

\[
\gamma_m = (\sigma^2_m X + \frac{4BRW_1X^2}{W_2} + \frac{12BRW_1X}{PW_2}) (1 + \frac{BRW_1}{W_2})
\]

\[
\quad + \frac{4X^2}{P} (1 + \frac{BRW_1}{W_2})^3 + \frac{12X}{P^2} (1 + \frac{BRW_1}{W_2})^3 + \frac{6BRW_1X}{W_2^3}.
\]

(42)
If $P \gg 1$ and $XBRW_1 = 2$ to 10, the variance and the skewness can be approximated, respectively, by

$$
\sigma^2_m = X^2 \left(1 + \frac{BRW_1}{W_2}\right)^2 \quad (43)
$$

and

$$
\gamma_m = 2X^3 \left(1 + \frac{BRW_1}{W_2}\right) \quad (44)
$$

Figures 20 and 21 show the errors of equations (43) and (44) in approximating equations (41) and (44) when $XBRW_1 = 6$, $W_2 = 0.1333$, and $P = 250$. The error of mean is zero, the error of variance is around 15%, and the error of skewness is about 30%. When $XBRW_1$ increases, the error of variance decreases and approaches zero. However, the error of skewness will increase and approach 100%. Given different $W_2$ and $P$ values, the errors will change. However, within certain ranges of values for $XBRW_1$, $W_2$, and $P$, the errors are acceptable.

In a similar way, the moments for the immobile water component (under the condition $XBRW_1 \gg W_2$) were derived, as follows:

$$
\mu_{\text{im}} = \frac{BRW_1 X}{W_2} \left(\frac{W_1}{W_2}\right) \quad (45)
$$

$$
\sigma^2_{\text{im}} = \left(\frac{BRW_1 X}{W_2}\right)^2 \left(\frac{W_1}{W_2}\right) \quad (46)
$$

and

$$
\gamma_{\text{im}} = 2\left(\frac{BRW_1 X}{W_2}\right)^3 \left(\frac{W_1}{W_2}\right) \quad (47)
$$

It is easy to show that moments of the response function for a two-parameter gamma distribution in the form of $y = (b^{a+1} x^a e^{-bx})/\Gamma(z + 1)$ are

$$
\mu = \frac{a}{b}, \quad \sigma^2 = \frac{a}{b^2}, \quad \gamma = \frac{2a}{b^3} \quad (48)
$$

Comparing them with equations (40) and (43) through (47), we immediately see the relationship between the parameters of the gamma distribution and the physical parameters in the two-component model. For the mobile water component we have,

$$
am_m = 1, \quad bm = \frac{W_2}{X(W_2 + BRW_1)} \quad (49)
$$

and for the immobile water component,
Since $W_1 \gg W_2$, we observe that the value of $b_{im}$ is very close to the value of $b_m$.

Figure 22 illustrates two impulse response functions, one for the white-box model, which is equivalent to the two-component model as aforementioned, the other for the grey-box model. Although there are some differences between the two caused by the errors in variance and skewness, they agree very well.

For a conservative chemical, chloride, Liu (1988) was also able to calculate and compare the moments of a physically based model and a grey-box model with a log-normal distribution.

\begin{align}
a_{im} &= \frac{W_1}{W_2}, \quad b_{im} = \frac{W_2}{(XBWR_1)}. \quad (50)
\end{align}
He also found that the agreement of moments between the two types of models was very satisfactory (Liu 1988).

By deriving the relationship between the parameters of the two models and comparing the moments of the impulse response functions, we have proven the consistency between the two models. This relationship theoretically gives us a way to obtain the parameters of the gamma distribution if the water content, sorption coefficient, and dispersion coefficient are known, although in an actual application of the grey-box model, the parameters of the response function are determined by curve fitting. We think the curve-fitting way is more pragmatic and convenient.

In the above consistency analysis, three conditions were specified: P (Paclet number) $>> 1; W_1 >> W_2; \text{ and } XBRW_1 = 2 \text{ to } 10. The first two were met in the field situation. A high ratio of $W_1/W_2$ indicated that the solute was inactivated quickly by either being mixed with immobile water and/or being adsorbed on the surface of soil particles, and that the solute was reactivated slowly upon reentering mobile water after the concentration of mobile water dropped. The second condition is the major reason there is good consistency between the two models. The third condition was set for satisfying the approximate equality of the skewness of the two models. It can be relaxed to be $XBRW_1 >> 2. The relaxed condition can be satisfied easily for soils with high immobile water content or high adsorptivity. The relaxing of this
condition will result in a higher variance and skewness of the impulse response function in the white-box model than in those given in equations (43) through (48). If the third condition cannot be met, use of a generalized gamma distribution or log-normal distribution is recommended.

**DISCUSSION**

Hydrodynamic transport mechanisms of either conservative or nonconservative chemicals in a soil with a steady-state flow regime can be simulated with both physically based and linear system models. In a physically based model, various mechanisms are represented by mean pore-water velocity, dispersion coefficient, and so forth. In a linear system model, these mechanisms may be represented by a particular probability distribution function of the pore-water velocity.

In the grey-box model, the impulse response function of the system is considered a probability density function. The form of this probability density function can be determined semianalytically or semiempirically. Although we do not quantitatively understand all physical mechanisms governing the solute transport phenomenon, this density function implicitly expresses the overall effects of those mechanisms.

In the simulation of the Fenamiphos transport at the Kunia site, gamma distribution was used as the impulse response function in the grey-box model. Another probability density function, log-normal distribution, was used by Jury (1982) to simulate the conservative solute transport in soils. The use of log-normal distribution was based on the assumption of plug water flow in individual vertical soil channels. In different channels, water velocity distribution varies and follows the log-normal distribution. Jury's application was rather successful. However, log-normal distribution cannot accommodate lateral solute movement phenomena occurring in Hawaiian aggregated soils, which retains solute in the soil pores, holding the solute in the topsoil for a long period.

Comparing simulated and measured Fenamiphos concentrations in Figure 23, it can be said that both models can satisfactorily simulate solute transport in soil. The performance of the grey-box model in the simulation of Fenamiphos concentration is better at deeper layers than at upper ones, while the white-box model better agrees with the measured data through the entire range of depths. For chloride, a conservative chemical, Liu (1988) was able to show that the grey-box model performed very well.
CONCLUSIONS

Mathematical simulation of solute transport in unsaturated soils can be accomplished using physically based and system approaches. A physically based model is generally in the form of a convection-dispersion equation, with a number of parameters representing relevant hydrodynamic and reaction mechanisms. A system model generally takes the form of an integral series in which overall effects of transport mechanisms are represented by response functions.

In this study, a two-component solute-soil system with steady-state flow was studied using the conjunctive application of two modeling approaches. The impulse response function of the linear system model was evaluated using a combination of methods: system parameterization (grey box) and physical parameterization (white box). The close agreement of the impulse response functions derived with the two modeling approaches proved that the approaches were compatible.
The scale effect of heterogeneity on the dispersion coefficient was mathematically shown in a previous study (Liu 1988). Owing to this effect, a commonly used one-dimensional convection-dispersion solute transport model with a constant dispersion coefficient would underestimate the solute spreading when the plume moved into deeper soils. This problem is avoided in the linear system approach by excluding an explicit dispersion term from its impulse response function.

According to Taylor (1953), a one-dimensional convection-dispersion equation becomes a valid solute transport model only after the establishment of a simple balance between the longitudinal convective solute transport and the cross-sectional diffusive transport. The initial mixing zone required for the establishment of this simple balance was estimated by previous research in solute transport in soils to be several hundred meters (Bresler and Dagan 1979), an estimate that was confirmed by our study. Thus, a serious question is raised regarding the applicability of a one-dimensional convection-dispersion model with a constant dispersion coefficient. Again, this problem does not exist in the linear system approach.

The use of log-normal or gamma distribution has been verified by the field data for different solute-soil systems. Our recommendation is that a log-normal distribution is suitable for a conservative solute; gamma distribution is more suitable for a reactive solute because all the lateral movement, such as bypassing, sorption, and decay, etc., are lumped in parameters $a$ and $b$ of the gamma distribution. A linear system model with a log-normal impulse response function produces a skewed normal concentration curve (Liu 1988), while a system with a gamma impulse response function has a less regular curve.

The conjunctive application of the white-box model and the grey-box model allows us to benefit from both models by gaining more insight into the solute transport process. The consistency of the two models was confirmed by comparing the mean, variance, and skewness of their impulse response functions. The comparison allows us to determine the mathematical relationship between the parameters of the soil transport system and those of the probability density function.

It is likely that models will be used increasingly as a management tool to predict the fate of chemicals in soils. The linear system model, especially the grey-box approach, has proven to be useful in simulating solute transport in heterogeneous soils. The simple form of the model and the small amount of data required make it suitable for the managerial purposes of evaluating the variation and distribution of either conservative or nonconservative solute in soil and its leaching into groundwater aquifers. In combination with Geographic Information System packages, it may prove to be more valuable for spatial evaluation of the distribution of contaminants with depth. Compared to the crude index method that has been used (Khan and
Liang 1989), the system approach provides better estimation of solute distribution in the soil and hence enhances the accuracy of prediction.

REFERENCES CITED


Schneider, R.C., and Green, R.E. 1989. Field movement and persistence of Fenamiphos in drip irrigation pineapple soils. Dept. of Agronomy and Soil Science and Dept. of Plant Pathology, University of Hawaii at Manoa, Honolulu.


