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¹² ABSTRACT (PURPOSE, METHOD, RESULTS, CONCLUSIONS) Groundwater contamination caused by residuals of agricultural chemicals and leachates from solid waste landfill sites is now one of the most critical environmental problems. Regulatory decisions regarding the use of agricultural chemicals and the control of the solid waste disposal require an understanding of the behavior and fate of residue chemicals in a subsurface environment. To meet this requirement, mathematical models that predict the pollution potential of groundwater contamination caused by various forms and amounts of waste inputs are commonly used as important management tools. Mathematical models have been traditionally formulated by following a physically based approach. The amount of chemicals within a transport volume is determined by mass flux into and out of the volume, and by kinetics of production and reduction within the volume. Relevant hydrodynamic characteristics and reaction kinetics are represented by specific model parameters. These parameters are then incorporated in a mathematical structure based on the mass conservation principle. The successful application of physically based models are often limited because of difficulties in solving the interrelated problems of parameter identification, system boundary definition, and mathematical solution. These problems can be largely alleviated by an alternative modeling approach which was developed based on a system theory. By following the system approach, dynamic relations between the chemical input at the soil surface and its subsequent downward movement are represented by system response functions that do not require knowledge of the intimate structure of relevant transport mechanisms. Techniques developed in this study were applied in the simulation of the transport of residuals of the pesticide DBCP in soils in the Kunia area of central Oahu, Hawaii, after an accidental spill of the chemical in April 1977. As a result, compatibility of the system modeling approach and a physically based modeling approach is demonstrated. This study also illustrates the computational superiority of the system modeling approach, especially for chemical residual transport in an aggregated soil where a bypassing phenomenon is obvious.	

AUTHORS:

Dr. Clark C.K. Liu
Associate Professor
Department of Civil Engineering
University of Hawaii at Manoa
2540 Dole Street, Holmes Hall 345
Honolulu, Hawaii 96822
Tel.: (808) 948-7658

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

**CHEMICAL RESIDUALS TRANSPORT IN AGGREGATED SOILS:
Mathematical Simulation by the Linear System Approach**

Clark C.K. Liu
Jing-Song Feng

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Project Completion Report
for
Dynamic Simulation of Solute Transport in
Soil by a Linear System Approach
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WATER RESOURCES RESEARCH CENTER
UNIVERSITY OF HAWAII AT MANOA
Honolulu, Hawaii 96822

ABSTRACT

Groundwater contamination caused by residuals of agricultural chemicals and leachates from solid waste landfill sites is now one of the most critical environmental problem. Regulatory decisions regarding the use of agricultural chemicals and the control of the solid waste disposal require an understanding of the behavior and fate of residue chemicals in a subsurface environment. To meet this requirement, mathematical models that predict the pollution potential of groundwater contamination caused by various forms and amounts of waste inputs are commonly used as important management tools.

Mathematical models have been traditionally formulated by following a physically based approach. The amount of chemicals within a transport volume is determined by mass flux into and out of the volume, and by kinetics of production and reduction within the volume. Relevant hydrodynamic characteristics and reaction kinetics are represented by specific model parameters. These parameters are then incorporated in a mathematical structure based on the mass conservation principle. The successful application of physically based models are often limited because of difficulties in solving the inter-related problems of parameter identification, system boundary definition, and mathematical solution. These problems can be largely alleviated by an alternative modeling approach which was developed based on a system theory. By following the system approach, dynamic relations between the chemical input at the soil surface and its subsequent downward movement are represented by system response functions that do not require knowledge of the intimate structure of relevant transport mechanisms.

Techniques developed in this study were applied in the simulation of the transport of residuals of the pesticide DBCP in soils in the Kunia area of central O'ahu, Hawai'i, after an accidental spill of the chemical in April 1977. As a result, compatibility of the system modeling approach and a physically based modeling approach is demonstrated. This study also illustrates the computational superiority of the system modeling approach, especially for chemical residual transport in an aggregated soil where a bypassing phenomenon is obvious.

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INTRODUCTION

A mathematical model can be defined as a set of equations that, for certain conditions and purposes, formulates and describes a prototype system. In a groundwater quality investigation, two primary purposes of a solute transport model are the interpretation of field data and the prediction of potential soil and groundwater pollution caused by agricultural pesticides and land disposal of hazardous wastes.

The behavior and fate of chemical residuals in soils and the underlying rock formation depend on hydrodynamic mixing processes of water movement and dispersion, and on reaction kinetics of relevant physicochemical and microbiological processes. A mathematical model, which is developed to relate chemical input to subsequent residual distribution, must be able to describe the dynamic response of the soil system due to all relevant processes.

In general, solute transport modeling can be conducted by following the physically based or system approach. In the physically based approach, relevant processes are represented by model parameters, whereas in the system approach, the overall effect of these processes is described by the model response function.

Physically Based Modeling Approach

Solute transport models have been traditionally developed by a physically based approach. Models thus developed take the form of partial differential equations that describe various dynamic components of a natural soil-solute system and their joint action on solute transport. The complexity of physically based solute transport models varies depending on the number of simplifying assumptions that are imposed in the model formulation. A complex, physically based model can be formulated based on coupled flow and solute transport equations. The most commonly used model, however, consists of a one-dimensional solute transport equation with steady-state flow.

Governing equations of physically based solute transport models include a number of parameters that represent relevant hydrodynamic and kinetic reaction mechanisms taking place in the soil-solute system. Estimating the values of parameters is a major modeling task (Fig. 1). Solution of model governing equations may be achieved by either analytical or numerical methods. Numerical methods, such as finite-difference or finite-element, are normally applied except when analytical solutions can be applied for simpler boundary and initial conditions.

The successful application of a physically based model is often confronted with one or more of the following problems.

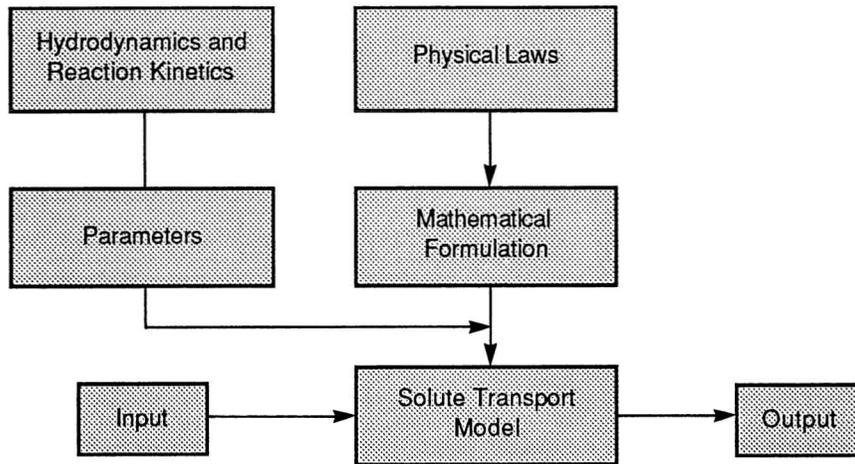


Figure 1. Solute transport modeling by a physically based approach

FLOW HYDRAULICS AND KINETIC REACTION REPRESENTATION. In the governing differential equations for a physically based model, hydrodynamic characteristics and reaction kinetics of a natural soil system are represented by specific parameters, such as permeability, dispersion coefficient, adsorption coefficient, and decay rate constant. These parameters are derived empirically or are sometimes partially conceptual. Thus, the representation of flow hydraulics and kinetics reactions is necessarily an incomplete one. This constitutes an inherent weakness as the validity of such simplifications can hardly be established in any standard modeling analysis.

PARAMETER IDENTIFICATION. Hydrodynamic and reaction kinetics parameters are determined from experimental data, an exercise commonly called parameter identification. A parameter value determined by laboratory experiments is not truly indicative of the particular mechanism it represents because it is difficult to isolate the effect of a single mechanism in terms of experimental observations. For example, the laboratory observations used to identify the adsorption coefficient may include the effects of molecular diffusion, biodegradation, and volatilization. The empirical nature of the model is further increased when parameter values identified in laboratory experiments are used to represent dynamic processes in the field.

DEFINITION OF SYSTEM BOUNDARIES. Mathematical modeling by a physically based approach is essentially that of boundary values. Modeling results are affected by the manner in which the system boundary and initial conditions are defined. In a simple convection-dispersion model, these conditions are simplified to allow a ready analytical solution. Varying degrees of simplification of actual boundaries are also required to solve model equations by numerical methods. However, simplifications of system boundaries can often lead to uncertainties in modeling results.

HETEROGENEITY AND SCALE EFFECT. Hydrodynamic and transport mechanisms in a field soil exhibit large spatial variations or spatial heterogeneity. Besides a single-cell model which computes solute concentration averaged for the entire system, spatial heterogeneity of field soils produces scale effects that cannot be easily incorporated into a physically based model (Sposito, Jury, and Gupta 1986).

System Modeling Approach

Modeling of solute transport in unsaturated soils can be accomplished alternately by a system approach. By following this approach, dynamic relations between the solute input in soil surface and its subsequent downward movement are constructed on the phenomenological grounds of the theory of hereditary processes. This technique was introduced by Volterra in an attempt to include hysteresis effects in the models of electromagnetism and elastic phenomena (see Distefano 1974, pp. 307-310).

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, depend on the entire history of a soil system. Mathematically, it can be described as

$$Q_o(t) = F \left[\int_{-\infty}^t Q_i(\tau) d\tau \right] \quad (1)$$

where in solute transport modeling, Q_i is the rate of chemical entry into the soil, Q_o is the rate of loss of chemical residual from the soil, and F a functional of Q_i .

In general, (1) can be expressed as a Volterra integral series that consists of linear and nonlinear elements. If the soil system is assumed linear, superposition character would require (1) to take the form of

$$Q_o(t) = \int_{-\infty}^t Q_i \cdot h(t, \tau) d\tau \quad (2)$$

where h is the impulse response function and for a time-invariant system, only a function of $t - \tau$.

The linear system approach was successfully applied in the modeling of the rainfall-runoff process of a watershed by Dooge (1973).

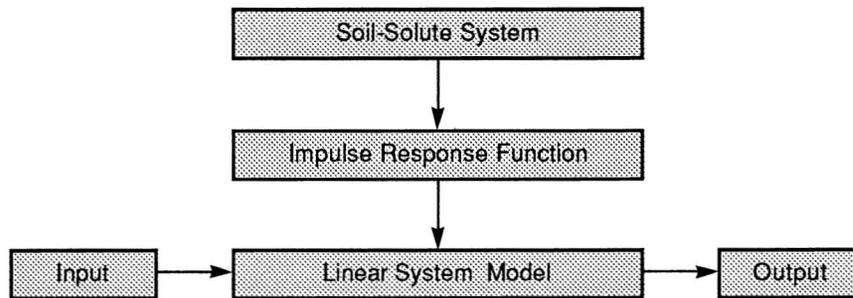


Figure 2. Solute transport modeling by a linear system approach

The system approach as shown in Figure 2 has been used in a few recent studies of solute transport in unsaturated and saturated soils by Duffy and Gelhar (1985); Jury, Esposito, and White (1986); and Liu (1988). These studies derived the impulse response in (2), relative to a few commonly used physically based models.

In its traditional application, equation (2) has been used as a deterministic model. In other words, the system response and input/output functions are considered as following a definite law of certainty, but not any law of probability. If any of the variables in the mathematical expression of a solute transport model is described by a probability distribution, the model is regarded as stochastic. Jury, Esposito, and White (1986) showed that (2) can be used as a stochastic model by simply taking the solute input time (τ) and the solute life time ($t' = t - \tau$) in a soil system as two random variables. The impulse response function h can then be interpreted as a conditional probability density function, or the probability that the solute input at time τ would remain in the soil system for time t' .

In this report, only the formulation and application of a deterministic linear system model are presented. Results of a preliminary investigation of stochastic solute transport modeling were presented in a related paper (Liu 1987).

OBJECTIVES

Linear system analysis is introduced in this study as an alternative approach in the simulation of chemical residual transport in aggregated soils. The project was mainly conducted to demonstrate the following characteristics of this alternative approach:

1. Compatibility of the linear system modeling approach with the conventional, physically based modeling approach

2. Computational superiority of the linear system approach, which deals with integral equations, over the physically based approach which deals with differential equations
3. Applicability of the linear system approach in the simulation of chemical residual transport in aggregated soils where soil water consists of mobile and immobile components.

SYSTEM MODELS AND IMPULSE RESPONSE FUNCTION

Functional F in (1) is an analytical functional of the input function $Q_i(\tau)$ which, in turn, is an analytical function of τ . An analytical function can always be expanded into an integral power series which takes the following form (Volterra 1959):

$$Q_o(t) = Q_i(t) + \int_{-\infty}^t Q(\tau) \cdot h_1(t, \tau) d\tau + \int_{-\infty}^t \int_{-\infty}^t Q_i(\tau_1, \tau_2) \cdot h_2(t, \tau_1, \tau_2) d\tau_1 d\tau_2 + \dots \quad (3)$$

The first term on the right hand side, $Q_i(t)$ represents the transient state of the system. Forms of the kernels or response functions of the multiple integral expansion, i.e., $h_1, h_2 \dots$, determine the behavior of a nonlinear system. A truncated second-order Volterra series was used in a nonlinear analysis of watershed rainfall-runoff processes (Liu and Brutsaert 1978). The application of a higher order Volterra series model requires the evaluation of a number of response functions—a very difficult task. Therefore, in most engineering applications, only linear systems with negligible transient contribution are considered. As a result, the system equation takes a much simpler form as shown in (2).

Many techniques have been developed in the evaluation of the system impulse response function, or the linear kernel. Generally, it can be accomplished by three different methods: (a) system identification, (b) system parameterization, and (c) physical parameterization.

In the first method, the impulse response function is determined based on one set of known input and output data and, thus, it involves a problem of inversion. As the functional series of the Volterra model is essentially a smoothing operation, small errors of input and output data may result in large deviations of the computed impulse response function. To overcome these uncertainties, it is sometimes necessary to introduce system optimization techniques in the course of the identification (Liu and Brutsaert 1978), or to conduct frequency-domain analysis (Bras and Rodriguez-Iturbe 1985).

In the second method, the dynamic nature of solute transport processes is assumed to be partially known, whereby 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.

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

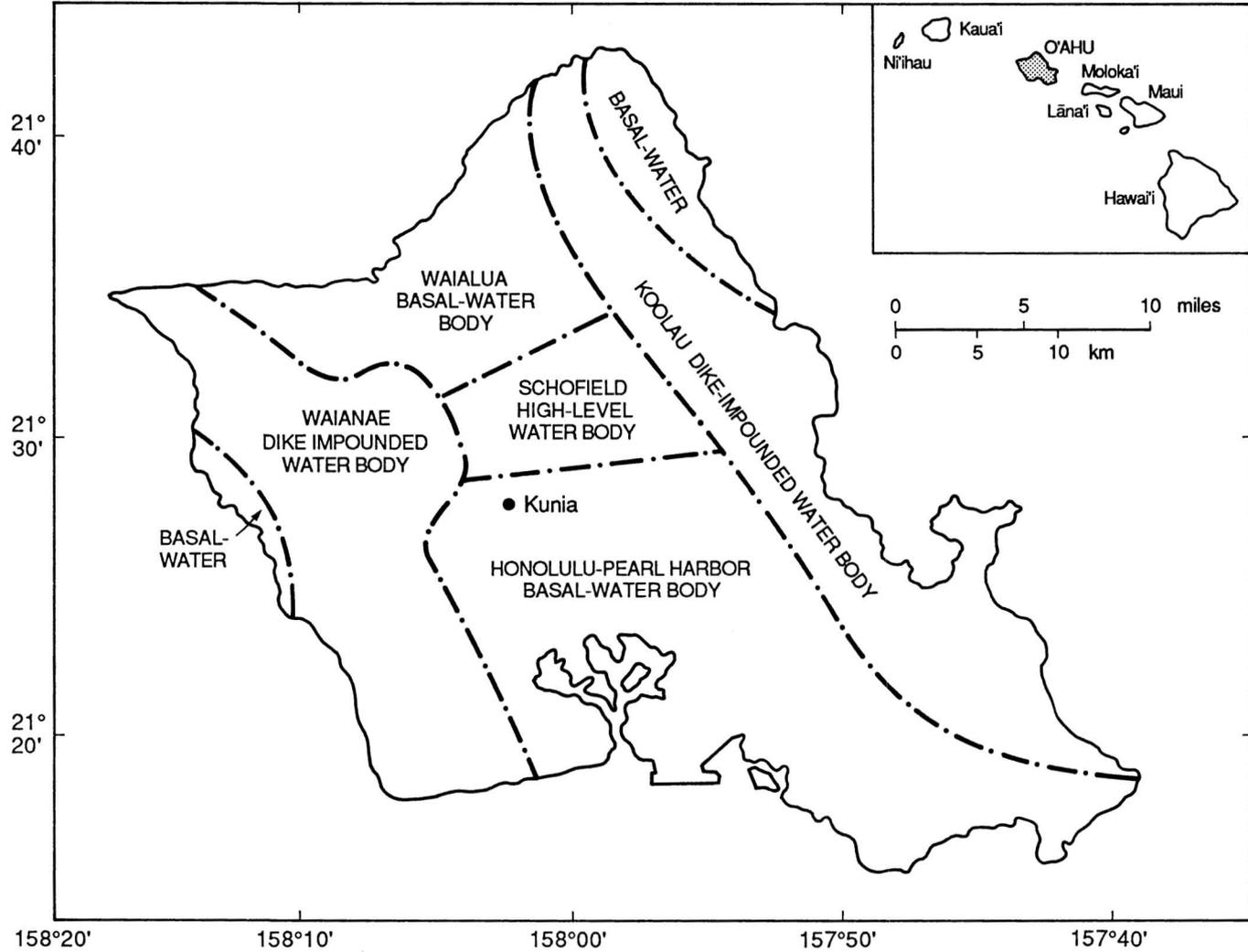
Therefore, in transport modeling, a physically based approach can be considered a special case of system approach. Ideally, a benefit of the system approach is fully realized by the conjunctive modeling approach which requires a simultaneous application of all of the above methods. As a first attempt, this study investigates the application of the system approach with the method of physical parameterization.

PESTICIDE RESIDUALS IN SOILS AND GROUNDWATER CONTAMINATION: THE KUNIA CASE

Part of an important pathway of the hydrologic cycle is the continuous percolation of water from the ground surface to the groundwater aquifer. Any contaminants that enter the recharge water on the ground surface and within the topsoils will eventually reach the groundwater, except the contaminant concentration that can be reduced to nondetectable levels by various decay processes.

Some potential groundwater contaminants are agricultural chemicals, land-disposed hazardous wastes, and leachates from septic tanks and landfill sites. In the state of Hawai'i, agricultural chemicals are the major concern of groundwater contamination (Lau 1985).

Tropical agriculture requires heavy use of herbicides, pesticides, and fertilizers. In the cultivation of pineapples, the soil fumigants dibromochloropropane (DBCP), ethylene dibromide (EDB), and dichloropropane-dichloropropene (DD) have been used extensively at one time or another in Hawai'i for more than 30 years (Lau 1985). Until 1980, these chemicals were thought to produce minimal environmental damage to the islands groundwater sources because of the islands' unique geologic and hydrologic features relative to the movement of soil water and groundwater (Figs. 3, 4). Figure 4 shows a typical geohydrological profile in the pineapple-cultivated area of central O'ahu. Before reaching the basal groundwater aquifer, residual chemicals must move through three distinct subsurface formations to a depth of about 300 m. Unfortunately, groundwater contamination by pesticides was only discovered in Hawai'i in 1980 (Mink 1981) when water samples collected from the Kunia Well on O'ahu



SOURCE: Liu et al. (1983).

Figure 3. Geomorphic provinces and Kunia spill site, O'ahu, Hawai'i

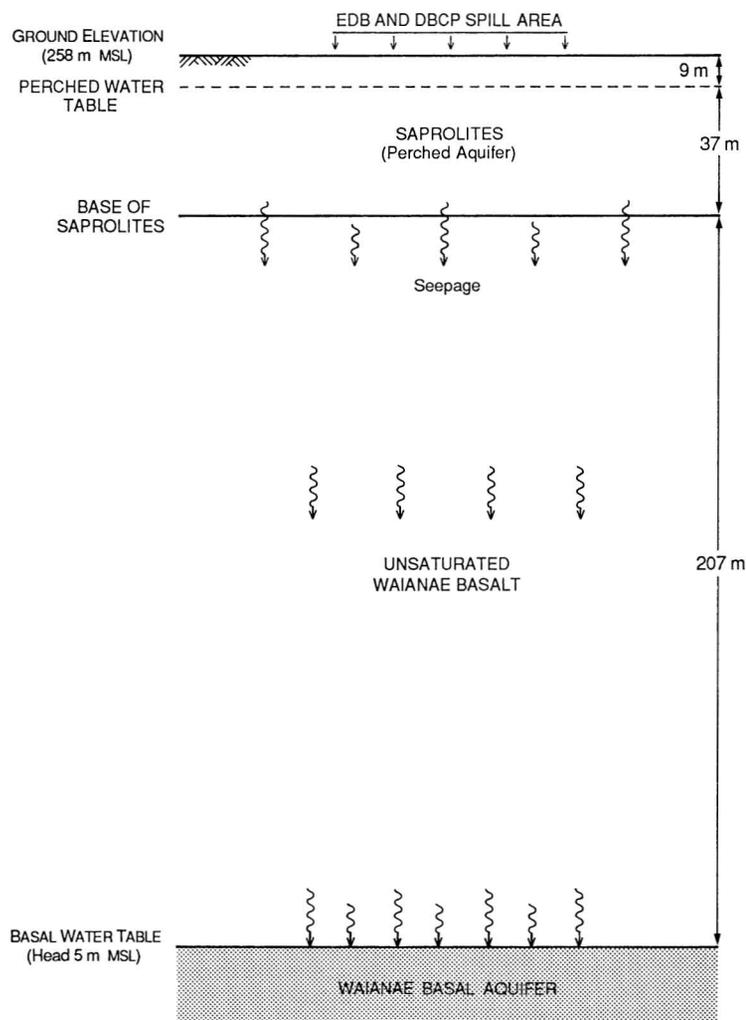


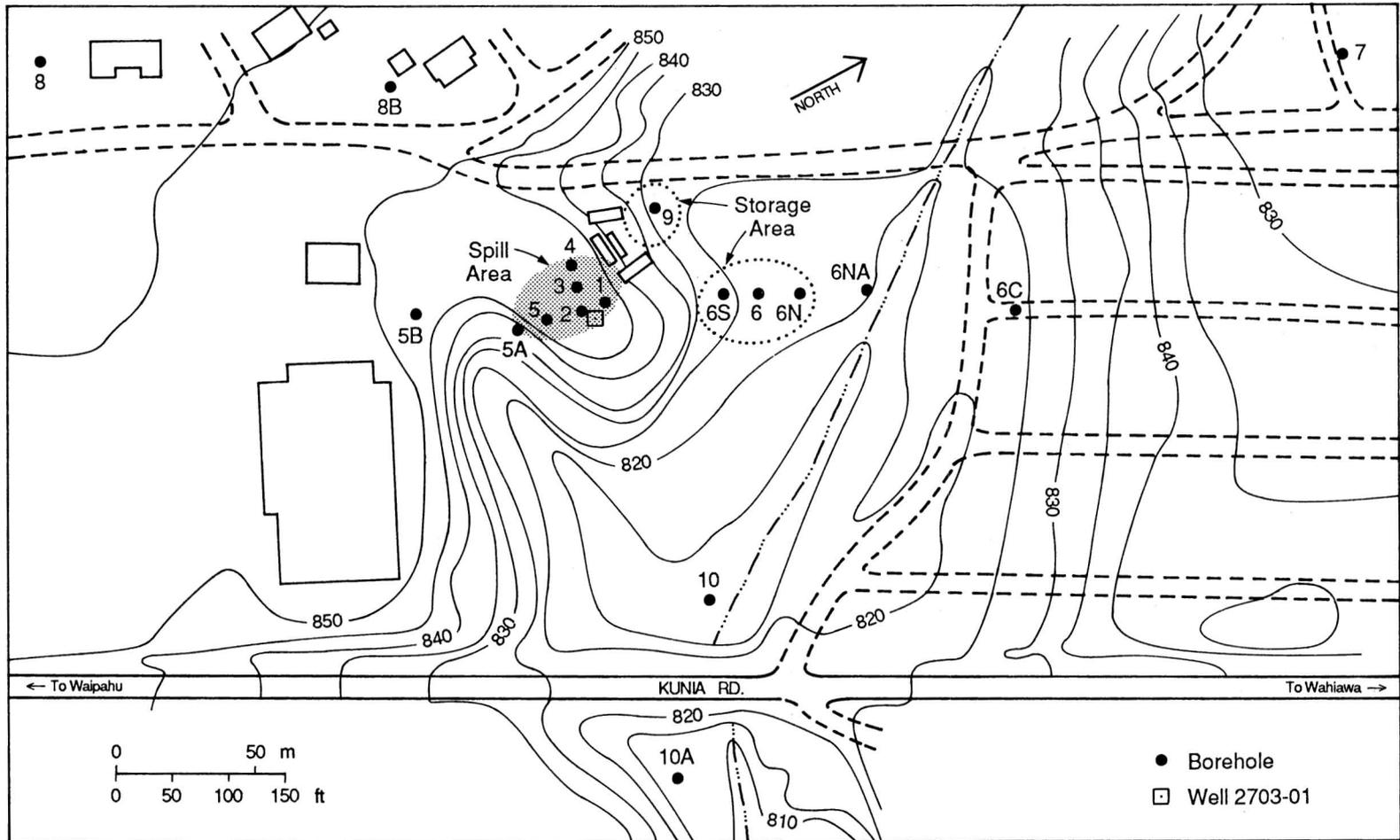
Figure 4. Geohydrological profile of Kunia spill area, O'ahu, Hawai'i

showed significant amounts of EDB ($92 \mu\text{g/l}$) and DBCP ($11 \mu\text{g/l}$). Since then, pesticide-related contaminants have been detected in several other wells in the basal waters of southern and central O'ahu aquifers.

Modeling techniques developed in this study will be used to study pesticide residual transport in soils of the Kunia area in central O'ahu.

The Kunia Well (State No. 2703-01) is located within a large pineapple plantation and near a pesticide mixing and storage facility operated by Del Monte Corporation (Fig. 5). Over the years EDB and DBCP were mixed and applied on pineapple fields on O'ahu and on other islands.

When EDB and DBCP were first detected in water from Kunia Well on 14 April 1980, their presence was attributed to an earlier accidental spill. On April 1977, 495 gal (1.9 m^3) of EDB



SOURCE: Mink (1981).

NOTE: Contours in ft ($\times 0.3048 = \text{m}$).

Figure 5. Soil borehole, Well 2703-01, storage, and spill sites in Kunia, O'ahu, Hawai'i, September 1980

was accidentally spilled over an area of about 585 m² (6300 ft²) near Kunia Well. The spilled EDB contained about 0.25% DBCP as an impurity.

After the detection of pesticides in the Kunia Well water, the Hawaii State Department of Health closed the well and launched a large-scale program of soil borings. Samples were collected at seven soil borings in the spill area, four in the storage and mixing area, and seven on the periphery of contamination (Fig. 5). Most of these borings are more than 15.2 m (50 ft) in depth (Mink 1981).

Core samples from five bore sites in the spill area were analyzed by several laboratories. Results showed the presence of EDB and DBCP at various depths in the soil profile, while large amounts of the pesticides still remained in the top 0.5 m (1.6 ft). In some samples EDB concentration exceeding 70,000 µg/l was measured. In soil samples taken near the ground surface, DBCP concentration was as high as 250 µg/l. Generally, concentration decreased with increasing soil depth. A small amount of DBCP was found at the 40-m (131.2-ft) depth below the ground surface (Fig. 6).

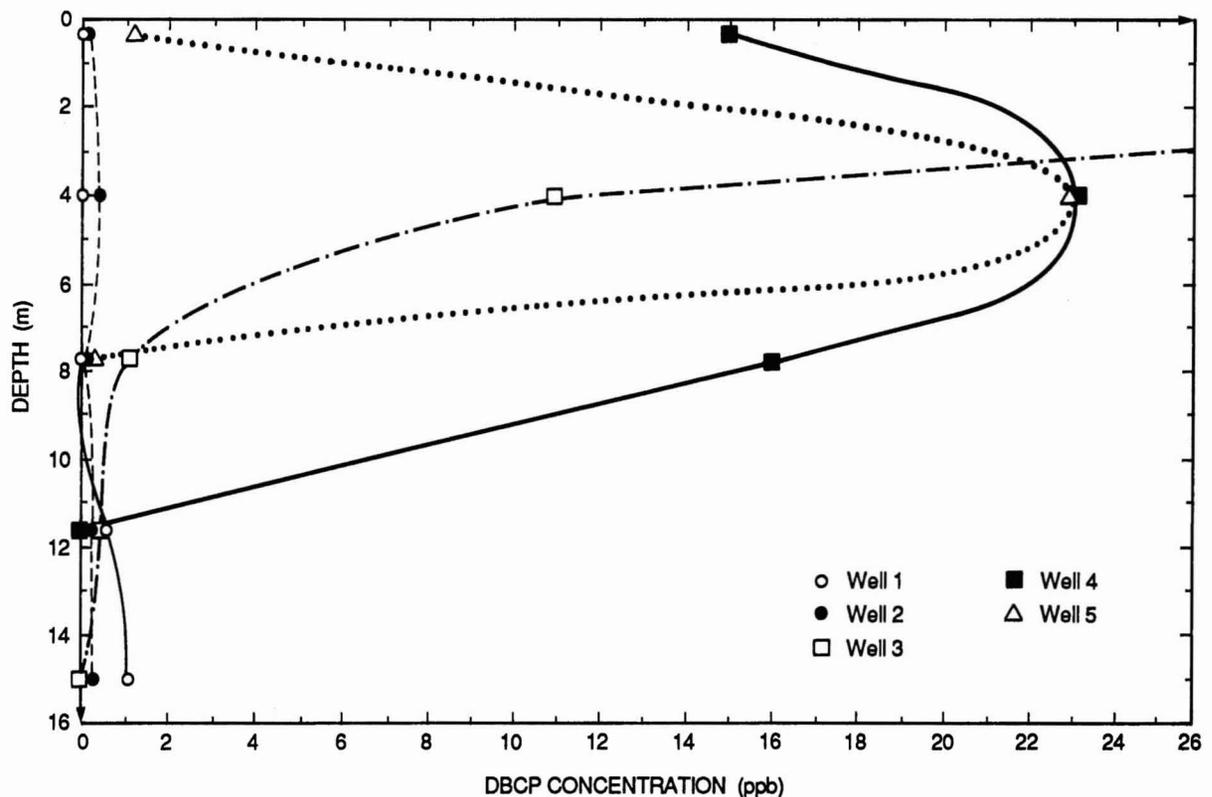


Figure 6. DBCP concentration in soils at Kunia spill area, O'ahu, Hawai'i

APPLICATION OF A SIMPLE LINEAR SYSTEM MODEL

For a soil system with steady-state water percolation, the rate of solute input and output, or Q_i and Q_o in (2) can be replaced by solute concentrations in water flowing into and out of the soil system, or C_i and C_o . Thus, (2) becomes

$$C_o(t) = \int_0^t C_i(\tau) \cdot h(t - \tau) d\tau \quad (4)$$

or in a Laplace domain, as

$$\bar{C}_o = \bar{C}_i \cdot \bar{h} \quad (4.1)$$

where \bar{C}_o , \bar{C}_i and \bar{h} are Laplace transformations of C_o , C_i and h , respectively. Note that the lower limit of integration is changed from $-\infty$ to 0 since the input starts at time $\tau = 0$. Equation (4), a simple linear system model of residual chemical transport in soils, indicates that the solute concentration at any soil depth can be calculated by a convolution operation of solute concentration in the inflow and the impulse response function of the soil unit at that depth. In this study, the impulse response function is derived by a method of physical parameterization. In other words, a simple convection-dispersion equation is first formulated, and the impulse response function of the corresponding linear system is then the solution of the convection-dispersion equation receiving a Dirac delta function input. The steady-state convection-dispersion equation used in a prior Kunia DBCP study (Liu et al. 1983) has the following form,

$$\left(1 + \frac{\rho K_D}{\theta}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} - K \left(1 + \frac{\rho K_D}{\theta}\right) C \quad (5)$$

where ρ is the soil bulk density (g/cm^3); θ the volumetric water content (cm^3 water/ cm^3 soil); C the DBCP concentration in solution ($\mu\text{g}/\text{cm}^3$ water); t , time (day); z the vertical space coordinate, positive in downward direction (cm); K the first-order decay coefficient (day^{-1}); K_D the adsorption coefficient (ml/g); the dispersion coefficient (cm^2/day); and V the water percolating velocity (cm/day).

Boundary and initial conditions associated with (5) are

$$C(z, t) = C_s e^{-\gamma t}, z = 0, t > 0 \quad (6)$$

$$C(z, t) = 0, z \rightarrow \infty, t \geq 0 \quad (7)$$

$$C(z, t) = 0, z > 0, t = 0 \quad (8)$$

where γ is the source decay coefficient (day^{-1}).

In the formulation of (5), instant equilibrium of pesticide residuals in solution and adsorbed on soil particles was assumed. Pesticide residuals in the gas phase are normally much smaller than that in solution or adsorbed by the soil matrix and can be ignored. Thus, the total pesticide residual concentration in soil, C_T , can be expressed as

$$C_T = (\rho K_D + \theta) C. \quad (9)$$

The net effect of the adsorption mechanism is to slow down the downward movement of pesticide residuals. Therefore the term $[1 + (\rho K_D/\theta)]$ in (5) is often called the retardation factor R . With the adsorption effect, the percolating velocity and dispersion coefficient are modified by the following relationships:

$$V_R = \frac{1}{R} V \quad (10)$$

$$D_R = \frac{1}{R} D. \quad (11)$$

With above definitions, (5) is simplified as

$$\frac{\partial C}{\partial t} = D_R \frac{\partial^2 C}{\partial z^2} - V_R \frac{\partial C}{\partial z} - KC. \quad (12)$$

Equation (12) with a Dirac delta function input can be readily solved by using the Laplace integral transformation method. For any time function $f(t)$, a Laplace integral transformation is defined as

$$F(s) = \int_0^{\infty} f(t) e^{-st} dt \quad (13)$$

where s is any number sufficiently large to converge the integral in (13). Based on the argument that st must be a pure number, s has units of t^{-1} . Thus, the Laplace transformation transforms the original function in the time domain into the frequency domain.

Taking the Laplace transformation of each term in (12), we have

$$D_R \frac{d^2 \bar{C}}{dz^2} - V_R \frac{d\bar{C}}{dz} - (K + s) \bar{C} = 0 \quad (14)$$

where \bar{C} is the transformed concentration function. Equation (14) is an ordinary differential equation with a constant coefficient. Its solution can be derived as

$$\bar{C} = \bar{C}_i \exp \left[\frac{V_R}{2D_R} z - \left(\frac{V_R^2}{4D_R} + \frac{K+S}{D_R} \right)^{1/2} z \right] \quad (15)$$

where \bar{C}_i is the Laplace transformation of input function. The Laplace transformation of the Dirac delta function is unity; thus according to (4.1), the Laplace transformation of the impulse response function (or transfer function) is

$$\bar{h} = \exp \left[\frac{V_R}{2D_R} - \left(\frac{V_R^2}{4D_R} + \frac{K+S}{D_R} \right)^{1/2} \right] z. \quad (16)$$

By conducting a Laplace inversion, the impulse response function in time domain is shown as

$$h(t, z) = \frac{z}{(4\pi t^3 D_R)^{1/2}} \exp \left[-\frac{(z - V_R t)^2}{4D_R t} - Kt \right]. \quad (17)$$

The input function of the Kunia DBCP transport model can be taken as the time function of DBCP concentration on the ground surface, or

$$C_i(0, t) = C_s \exp(-\gamma t). \quad (6)$$

As a volatile chemical, DBCP residuals in soils near the ground surface may dissipate by volatilization, the main cause of source decay. Thus, the value of γ depends on a number of environmental factors that affect the rate of volatilization, such as organic matter content, soil moisture, adsorption, and temperature. The introduction of (6) and (17) into (4) gives the simple linear system model for DBCP transport in Kunia soils as

$$C = \int_0^t C_s \exp(-\gamma \tau) \cdot \frac{z}{(4\pi t^3 D_R)^{1/2}} \exp \left\{ -\frac{[z - V_R(t - \tau)]^2}{4D_R(t - \tau)} - K(t - \tau) \right\} d\tau. \quad (18)$$

Values of parameters that describe the hydrodynamic mixing and reaction kinetics of DBCP transport in Kunia soils were determined based on field and laboratory data (Liu et al. 1983). Results are summarized in Table 1. With these parameters, we determined the functions of input and impulse response. DBCP distribution in the Kunia soil over a 3-yr period after the accidental spill was then calculated by (18). The results are shown in Tables 2 to 4 and in Figures 7 to 9. The calculated and observed profiles of total DBCP concentration C_T at the end of three years are given in Figure 7.

Values of DBCP adsorption coefficients for Kunia soil were determined by a series of experiments conducted by Liu and others (1983) who found that the ability of soil particles to adsorb DBCP in soil water is strongest near the ground surface where soil organic carbon content is high. Below a topsoil layer, soil adsorptive ability diminishes in relation to depth. The value of the adsorption coefficient used in this simple model is a weighted average in the total simulation depth, or 20 m.

DBCP may undergo slow degradation in soils in the presence of microorganisms. For two test fields on the island of Maui, the rate of degradation was found to be 0.00016 hr^{-1} in the top 0.45 m of soil and much slower for greater depths (Liu, Tamrakar, and Green 1987). In this study the value of biodegradation was taken to be zero.

TABLE 1. VALUES OF HYDRODYNAMIC AND REACTION KINETICS PARAMETERS

Parameter	Notation	Value
Percolating Velocity	V	1.16 cm/day
Dispersion Coefficient	D	2.40 cm ² /day
Soil Bulk Density	ρ	1.80 g/cm ³
Adsorption Coefficient	K _D	1.94 ml/g
Soil Water Content	θ	0.30 m ³ /m ³
Initial DBCP Concentration	C ₀	3480 μ g/l
Source Decay Coefficient	γ	0.005 day ⁻¹
Biodegradation Coefficient	K	0

SOLUTE TRANSPORT IN AGGREGATED SOILS

A simple system model, or (18) used in the calculation of the last section, is based on a conceptual formulation of a one-dimensional steady-state, advection-dispersion equation. Basic solutions of this equation with short duration input would take the form of a Gaussian distribution. Hence, according to this equation, a concentrated input of pesticide at the ground surface will move downward with a bell-shaped residual concentration profile. The peak of this predicted concentration profile diminishes as it moves downward with the percolating water. On the other hand, the width of the profile expands depending on the time of travel and the value of dispersion coefficient. This is shown in the calculated DBCP distribution (Fig. 7).

The use of (18) assumes that water percolates down through the soil profile at a uniform velocity. Generally, uniform percolation occurs only in homogeneous soils, such as uniform, fine sandy loam or carefully packed laboratory soil columns (Green 1984). Most field soils, however, are structurally nonuniform: pore-size distribution of soil is bimodal, with large pores between the aggregates and small pores in the aggregates or soil peds (DeSmedt and Wierenga 1979).

When a plume of contaminated water moves downward through an aggregated field soil, hydrodynamic mixing occurs principally in large pores because of advection and dispersion. Soil water in small pores remains stationary, but in large pores its solute concentration may change by lateral transfer. Therefore, in relation to solute transport in aggregated soils, soil water content may be divided into two components: a mobile component of soil water in large pores and an immobile component of soil water in small pores.

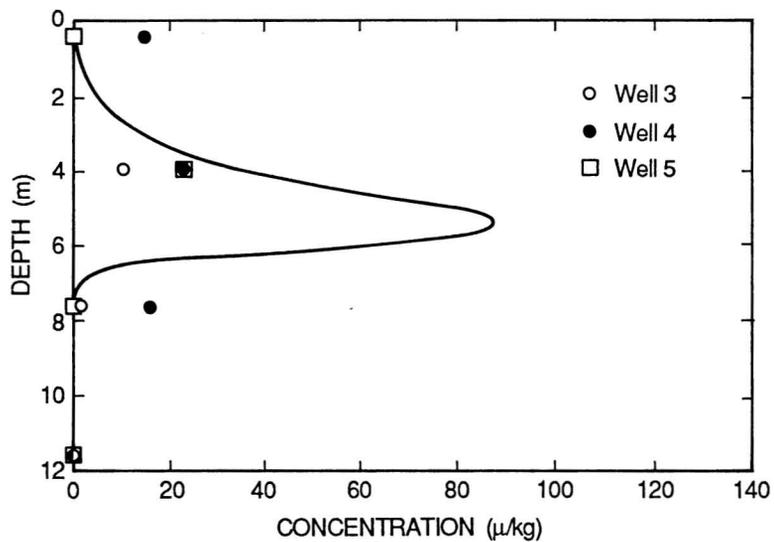


Figure 7. System model calculation and observation of total DBCP concentration in Kunia soil 3 yrs after April 1977 spill

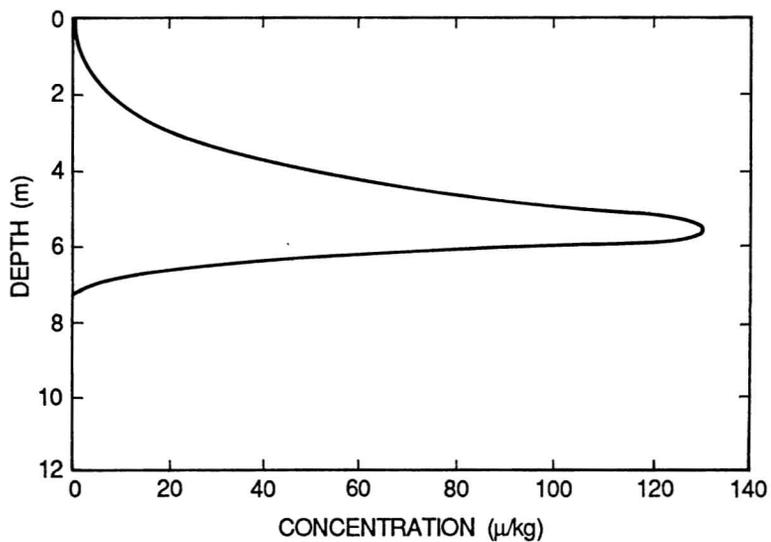


Figure 8. System model calculation of DBCP concentration in Kunia soil solution 3 yrs after spill

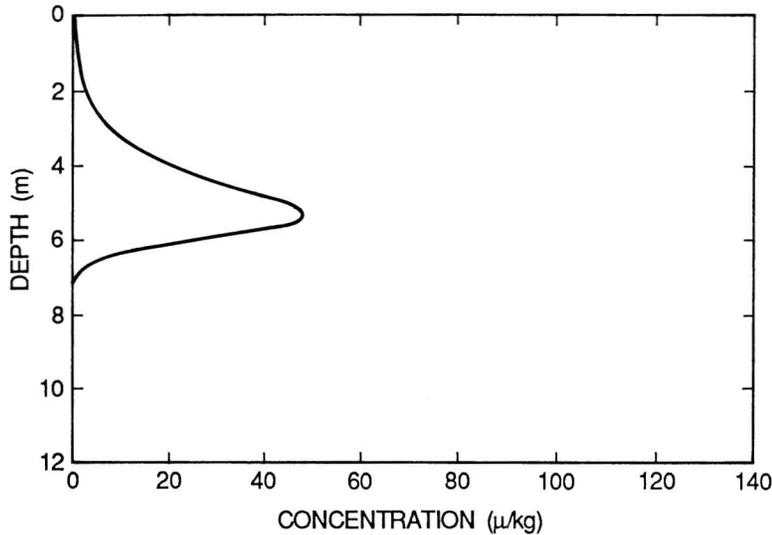


Figure 9. System model calculation of adsorbed DBCP concentration in Kunia soil 3 yrs after spill

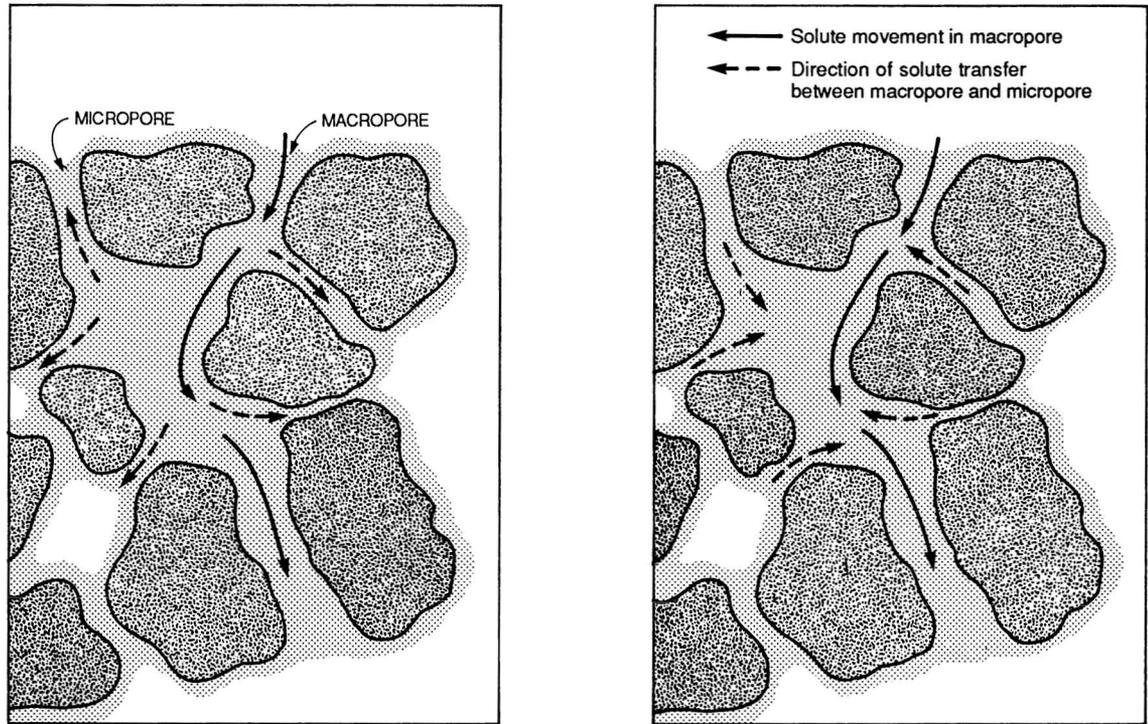
As indicated in Figure 10, aggregated soils produce a phase effect on solute transport. Figure 10.1 shows that, after a storm or irrigation event, a large amount of recharge-contaminated water infiltrates down in the soil and pushes some concentrated solution into small pores. A certain amount of solutes remains in small pores after the plume of contaminated water moves down through large pores. Subsequently, lateral transfer gradually releases solute back into the mobile water (Fig. 10.2). Therefore, two-component aggregated soils alter the original residual concentration curve into one with a long tail and even with multiple peaks. This is called the bypassing phenomenon (Green 1984; Green and Khan 1987).

Equation (5) is a linear equation in that actions of various transport mechanisms are superimposed to yield the final result. By modifying this simple model to take into consideration the phenomenon, the lateral transfer between mobile and immobile water in aggregated soils can be taken as an additional mixing mechanism. As a result, a coupled model would be formulated for aggregated soils. For the mobile component, the governing equation is the modified form of (5) with an additional term for lateral transfer. For the immobile component, the transport equation consists of only the lateral transfer. Details on model formation and application are given in the next section.

TWO-COMPONENT, MULTI-LAYERED LINEAR SYSTEM MODEL

Model Formulation

By adding the lateral-transfer term to (5), a transport model for the mobile component of solute, C_1 , in an aggregated soil can be formulated as



SOURCE: Green and Kahn (1987).

10.1. Recharge with contaminated water

10.2. Subsequent recharge with uncontaminated water

Figure 10. Solute transport through aggregated soils

$$(f \rho K_D + \theta_m) \frac{\partial C_1}{\partial t} + [\rho K_D(1-f) + (\theta - \theta_m)] \frac{\partial C_2}{\partial t} = D \theta_m \frac{\partial^2 C_1}{\partial z^2} - V_m \theta_m \frac{\partial C_1}{\partial z} \quad (19)$$

and for the immobile component of solute, C_2 , as

$$[\rho K_D(1-f) + (\theta - \theta_m)] \frac{\partial C_2}{\partial t} = \alpha(C_1 - C_2) \quad (20)$$

where θ_m is the mobile phase soil water content, f the fraction of total adsorption due to the mobile component, α the mass transfer coefficient between mobile and immobile water (day^{-1}), C_1 the solute concentration in mobile water ($\mu\text{g/l}$), C_2 the solute concentration in immobile water ($\mu\text{g/l}$), and V_m the percolation velocity of mobile water (cm/day).

Equations (19) and (20) can be expressed in terms of dimensionless time and distance variables (X , T) and other dimensionless parameters, which are defined by Sposito, Jury, and Gupta (1986) as

$$\begin{aligned}
X &= \frac{z}{L} & B &= \frac{\phi_m R_1}{R} & P &= \frac{V_m L}{D} \\
T &= \frac{Vt}{L} & R &= 1 + \frac{\rho K_D}{\theta} & W &= \frac{\alpha L}{V\theta} \\
\phi_m &= \frac{\theta_m}{\theta} & R_1 &= 1 + \frac{f \rho K_D}{\theta_m} & \frac{V_m}{V} &= \frac{1}{\phi_m}
\end{aligned}$$

Note that the pecllet number P as defined above gives the relative importance of convection and dispersion in solute transport.

With these definitions, dimensionless forms of (19) and (20) are

$$BR \frac{\partial C_1}{\partial T} + (1-B)R \frac{\partial C_2}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} \quad (21)$$

and

$$(1-B)R \frac{\partial C_2}{\partial T} = W(C_1 - C_2). \quad (22)$$

Model Solution

Taking the Laplace time transformation with respect to T on both sides of (21) and (22), two ordinary differential equations are formed:

$$\frac{1}{P} \frac{d^2 \bar{C}_1}{dX^2} - \frac{d\bar{C}_1}{dX} = BR S_1 \bar{C}_1 + (1-B)R S_1 \bar{C}_2 \quad (23)$$

and

$$(1-B)R S_1 \bar{C}_2 = W(\bar{C}_1 - \bar{C}_2) \quad (24)$$

where \bar{C}_1 and \bar{C}_2 are, respectively, transformed concentration functions of mobile and immobile water; and S_1 is the variable associated with the Laplace transformation.

Solution of (23), with a Dirac delta function input, can be readily derived as

$$\bar{h}_m(X, S_1) = \exp X \cdot \left(\frac{P}{2} - \frac{1}{2} \left\{ P^2 + 4BRPS_1 \left[1 + \frac{(1-B)W/B}{(1-B)RS_1 + W} \right] \right\}^{1/2} \right) \quad (25)$$

where \bar{h}_m is the Laplace transformation of the impulse response function (h_m) of a linear system model corresponding to (21). This linear system model takes the form of

$$C_m(X, T) = \int_0^T C_i(\zeta) \cdot h_m(T - \zeta) d\zeta \quad (26)$$

where ζ denotes the dimensionless input time.

According to the convolution theorem, convolution in the time domain corresponds to multiplication in the frequency domain. In other words, (25) may be expressed in the frequency domain as

$$\bar{C}_m = \bar{C}_i \cdot \bar{h}_m . \quad (27)$$

Hence, the transformed output function \bar{C}_m can be calculated by a simple multiplication of the transformed input function \bar{C}_i and the transformed impulse response function \bar{h}_m .

At the Kunia site, DBCP input function was developed in the last section, which can be expressed in a dimensionless form as

$$C_i = C_s \exp(-\gamma T) . \quad (28)$$

By a Laplace time transformation, it becomes

$$\bar{C}_i = \frac{C_s}{\gamma + S_1} \quad (29)$$

By introducing the results of computation by (23) and (29) into (27), the transformed output function, or DBCP concentration at a specific soil depth is obtained. This output function in time domain can then be calculated by a Laplace inversion, or

$$C_m(X, T) = L^{-1}(\bar{C}_i \cdot \bar{h}_m) \quad (30)$$

where L^{-1} denotes the inverse Laplace transformation.

Similarly, the Laplace transformation of the impulse response function for the immobile component is

$$\bar{h}_{im} = \frac{W}{(1-B)RS_1 + W} \cdot \bar{h}_m \quad (31)$$

and the output DBCP concentration in immobile water is

$$C_{im} = L^{-1}(\bar{C}_i \cdot \bar{h}_{im}) . \quad (32)$$

Impulse response functions h_m and h_{im} are functions of soil depth z (or a dimensionless depth $x = z/L$). If the soil is vertically uniform, the output solute concentration at any depth (z_d) can be calculated by replacing z with z_d .

The linear system model also allows analysis of a vertically nonhomogeneous soil, for example, where a soil consists of two distinct upper and lower layers. Equations derived above are still valid for the upper layer. In the lower layers, however, the system boundary condition and values of system parameters must be redefined.

According to the linear system theory, an impulse response function of a particular soil system depends on the actions of transport mechanisms and does not depend on the system

boundary condition. Therefore, impulse response functions for mobile and immobile water of the lower soil layer can be derived similarly to those of the upper layer. They are

$$\bar{h}'_m(X, S) = \exp(X - 1) \left(\frac{P'}{2} - \frac{1}{2} \left\{ P'^2 + 4BR'P'\beta S_1 \left[1 + \frac{(1-B')W/B'}{(1-B)\beta R'S_1 + W} \right] \right\}^{1/2} \right) \quad (33)$$

and

$$\bar{h}'_{im}(X, S_1) = \frac{W'}{(1-B)R'\beta S_1 + W'} \cdot \bar{h}'_m \quad (34)$$

where prime denotes the values for the lower layer and $\beta = \theta'/\theta$.

Output from the upper layer serves as input for the lower layer. Hence, for mobile water,

$$\bar{C}'_{im} = \bar{C}_m \cdot \bar{h}'_m \quad (35)$$

and

$$C'_{im} = L^{-1}(\bar{C}_m \cdot \bar{h}'_{im}) \quad (36)$$

where C'_m gives the solute concentration of mobile water in the lower layer and \bar{C}'_m is its Laplace transformation.

Similarly, for immobile water,

$$\bar{C}'_{im} = \bar{C}_m \cdot \bar{h}'_{im} \quad (37)$$

and

$$C'_{im} = L^{-1}(\bar{C}_m \cdot \bar{h}_{im}) \quad (38)$$

where C'_{im} gives the solute concentration of immobile water in the lower layer and \bar{C}'_{im} is its Laplace transformation. Note that the solute concentration at any depth in the lower soil layer can be calculated by (35) and (37) by simply specifying the required depth in the corresponding impulse response functions, or by (32) and (33).

Finally, the total residual chemical concentration in soil, C_T can be calculated by the following equations:

$$C_T = [BR C_m + (1-B)R C_{im}] \theta \quad (39)$$

$$C'_T = [B'R' C'_m + (1-B')R' C'_{im}] \theta'. \quad (40)$$

Model Application

Computer programs have been developed to calculate residual chemical concentrations in mobile and immobile waters and the total soil concentration (Apps. A, B).

The two-component, two-layered linear system model as derived above was used in the study of DBCP transport at the Kunia site. Values of dimensionless parameters are summarized in Table 5. The actual computations were conducted on an HP9000 in the College of Engineering, University of Hawaii at Manoa. Modeling results are shown in Tables 6 to 9 and Figures 11 to 14. Figure 14 is a three-dimensional plot of the changes of DBCP residuals in soils as a function of time and soil depth.

DISCUSSION

Transport of residual chemicals in Hawai'i soils is a result of several important mechanisms of hydrodynamic mixing and transformation, namely, convection, dispersion, adsorption, volatilization, and "bypassing". Convection is caused by the mean motion of the soil water. Dispersion is caused by the nonuniform percolation velocity distribution and molecular diffusion, of which the latter usually has a negligible effect in a field soil.

Organic chemicals in percolating water can be adsorbed by soil particles. And the adsorbed chemicals are released into future percolating water which contains less chemical concentration. Thus, adsorption essentially produces a retardation effect on downward movement of chemicals. A retardation factor R is conventionally defined and used to modify convective velocity and dispersion.

Net loss of residual volatile chemicals, such as DBCP from soil, is attributed to volatilization and, to a lesser degree, to biodegradation. In this study, the effect of volatilization is accounted for in terms of a source decay function. Biodegradation is taken to be negligible.

At first, a simple linear system model was formulated for DBCP transport in Kunia soil. The model includes the effects of convection, dispersion, retardation, and source decay. Calculated DBCP residual distribution is a bell-shaped Gaussian curve that progresses downward with time, while its peak reduces and the base width increases. DBCP residual concentrations in soil water, adsorbed by soil particles, and relative to the entire soil volume were calculated (Figs. 7-9). Also shown in Figure 7 are observed total DBCP residual concentrations based on soil samples collected at several bore sites at the Kunia spill site.

By comparing the calculated and observed results, it is obvious that a simple model is unsatisfactory because it fails to recognize all of the important mechanisms in its formulation and the change of transport characteristics in various soil layers.

Improvement of model formulation was later accomplished by dividing the soil water into mobile and immobile components and thus recognizing the bypassing phenomenon of an aggregated soil, and by dividing the soil system into layers and thus allowing the adsorption

TABLE 5. VALUES OF HYDRODYNAMIC AND KINETICS PARAMETERS FOR TWO-COMPONENT, TWO-LAYERED MODEL

PARAMETER	NOTATION	VALUE		NOTES
		Upper Layer	Lower Layer	
Percolating velocity	V	1.16 m/day	1.16 m/day	
Percolating velocity of mobile water	V_m	1.547 m/day	3.868 m/day	
Dispersion coefficient	D	2.40 m ² /day	2.40 m ² /day	
Soil bulk density	ρ	1.80 g/m ³	1.80 g/m ³	
Adsorption coefficient	K_D	1.94 ml/g	0.02 ml/g	
Soil water content	θ	0.30	0.30	
Soil water content in mobile phase	θ_m	0.225	0.09	
Mobile phase, volume factor	ϕ_m	0.75	0.3	
Mass fraction of mobile phase adsorption	f	0.75	0.3	
DBCP concentration in solution	C_o	275.32 μ g/l	275.32 μ g/l	
Source decay coefficient	γ	0.005 day ⁻¹	—	
Biodegradation coefficient	K	0	0	
Retardation factor	R	12.64	1.12	$R = 1 + \rho K_D / \theta$
Retardation factor in mobile phase	R_1	12.64	1.12	$R_1 = 1 + f \rho K_D / \theta_m$
Peclet number	P	32.23	80.583	$P = V_m L / D$
Retardation ratio	B	0.75	0.3	$B = \theta_m \cdot R_1 / R$
Mass transfer coefficient between mobile and immobile phases	α	0.1	0.1	
Dimensionless transfer coefficient	W	14.368	14.368	$W = \alpha \cdot L / (V_m \theta_m)$

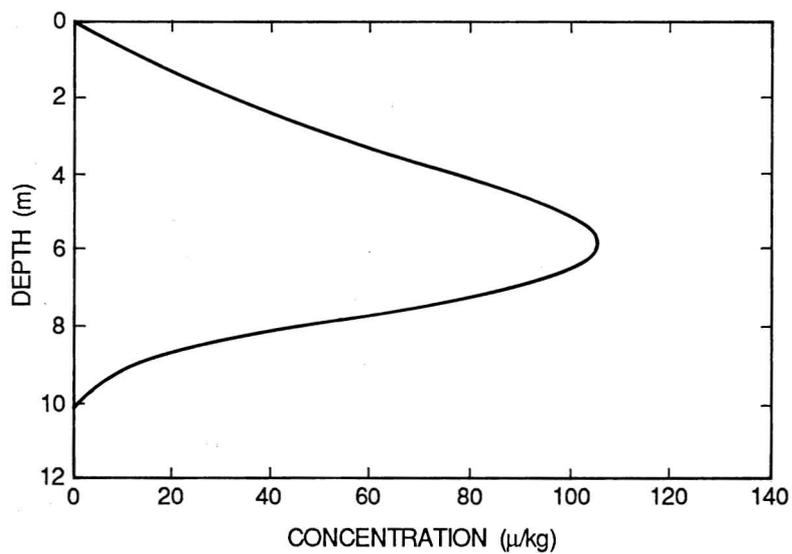


Figure 11. System model calculation of DBCP concentration in Kunia soil water 3 yrs after spill

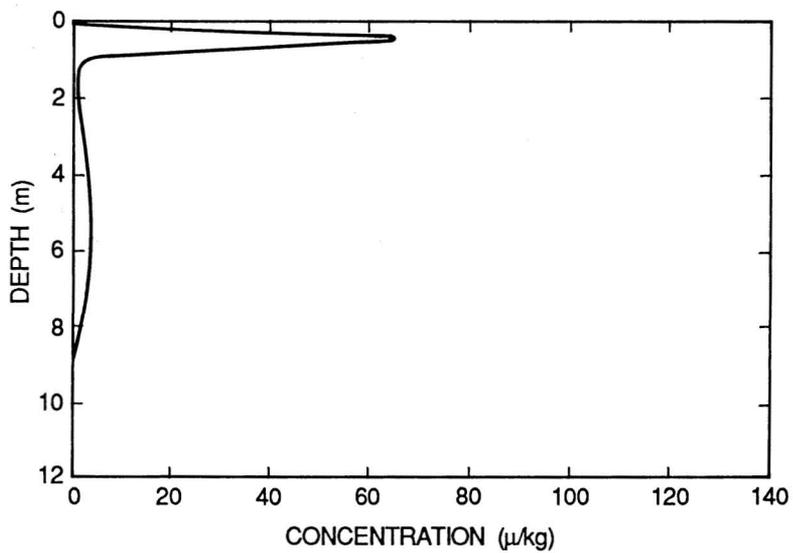
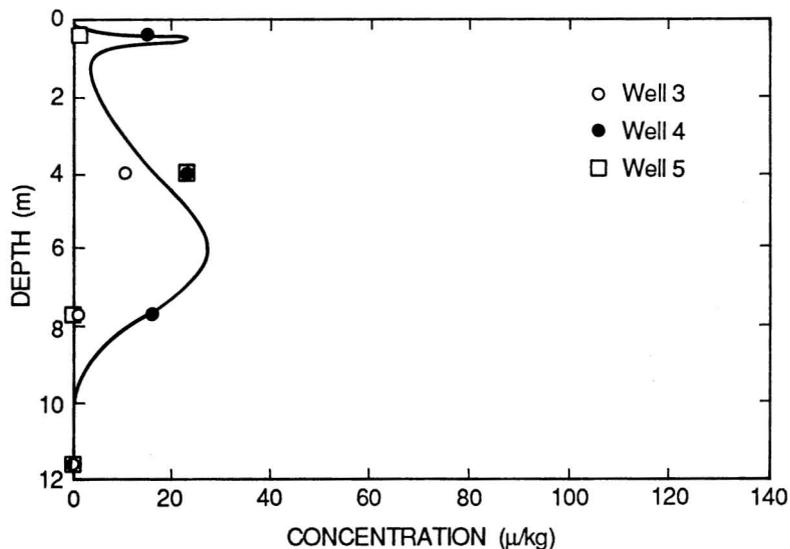


Figure 12. Two-component system model calculation of adsorbed DBCP concentration in Kunia soil water 3 yrs after spill



NOTE: Source decay coefficient $\gamma = 0.0075 \text{ day}^{-1}$.

Figure 13. Two-component system model calculation of total DBCP concentration in Kunia soil 3 yrs after spill

coefficient, soil water content, and other mixing properties to change vertically. With these modifications, a model with two coupled partial differential equations was formulated.

An analytical solution to the two coupled partial differential equation is difficult to derive. Methods of numerical solution, although applicable, would provide only an approximate answer and often be confronted with the problem of numerical dispersion.

In this study, a linear system approach is introduced again relative to a modified model, to demonstrate mainly its computational superiority. This modeling approach allows separate evaluation of the system impulse response function and the solute input function. After values of these two functions are evaluated, the output function, or the solute distribution in the soil, can be readily determined by a simple mathematical operation of convolution. More efficient computational procedures can be established by using techniques of frequency domain analysis. First, the impulse response function and the input function are evaluated in the frequency domain by a Laplace transformation of these functions. Output can then be calculated by a multiplication of the transformed impulse response function and the input function, followed by a Laplace inversion.

Linear system modeling of a two-component, two-layered soil system was applied to the Kunia site. Results are shown in Tables 7 to 9 and in Figures 11 to 14. Figure 13 indicates that a two-component, two-layered system representation can simulate rather closely the DBCP transport in the Kunia spill site during the 3-yr period after the accidental spill, in comparison with field sampling results. Calculated DBCP distribution in the Kunia soil at the end of three years after the accidental spill shows a higher residual concentration near the ground surface,

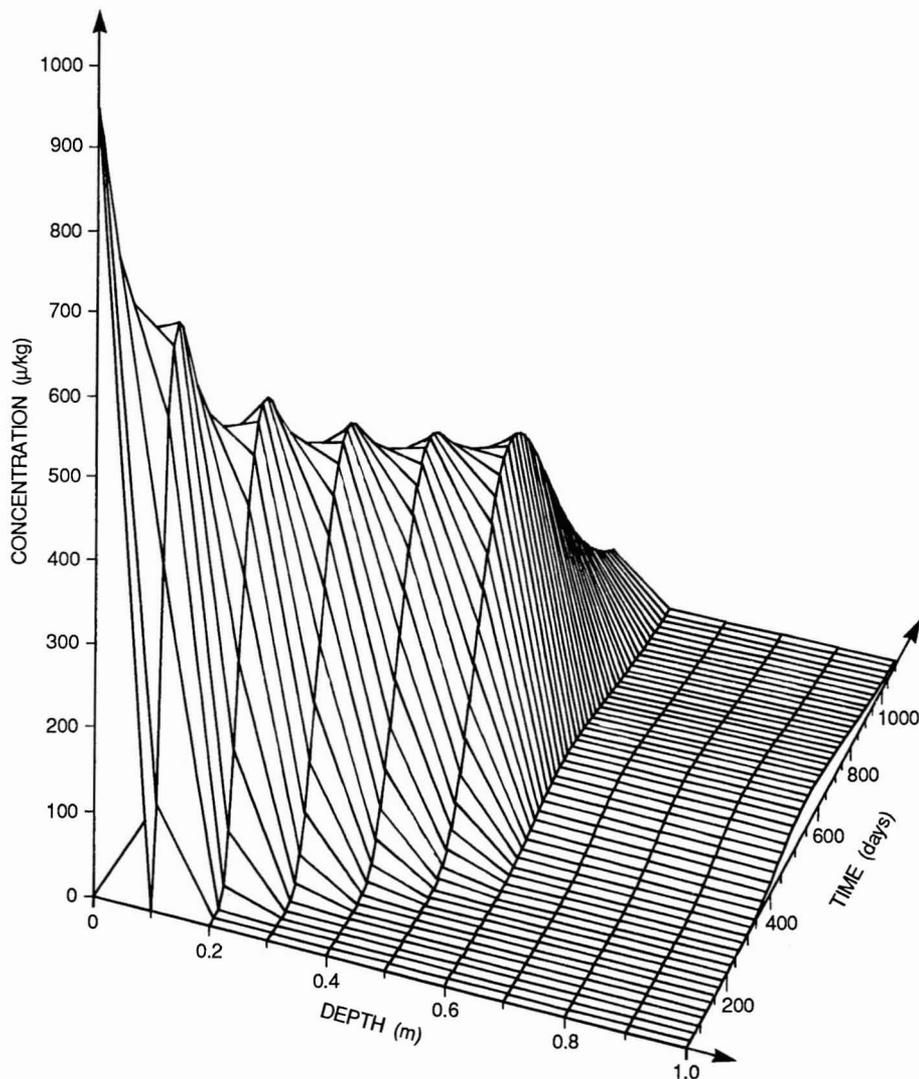


Figure 14. DBCP concentration vs. depth and time

and a second peak at about 6 m below the ground surface. These results are supported by field data. It should be noted that the model is a deterministic one and, therefore, gives only an averaged condition over any horizontal plane in the soil system. Lateral variations of observed residual concentration, caused mainly by spatial heterogeneity of the soil system, can only be investigated by a stochastic model. Stochastic soil transport modeling by a linear system approach is the subject of research currently underway at the University of Hawaii and elsewhere.

DBCP is a relatively volatile chemical. Volatilization of DBCP residual from soil to air determines, to a large degree, the chemical persistence in soil (Pringle, Liu, and Green 1984). In this modeling study, long-term volatilization loss of DBCP from the topsoil was represented

by a first-order source decay function. The value of the decay coefficient was taken as 0.005 day^{-1} . By increasing it to 0.0075 day^{-1} , the calculated DBCP residual concentration distribution shown in Figure 13 indicates that volatilization has a major impact on the amount of chemicals remaining in the soil, especially in soils near the ground surface.

Both predicted and observed DBCP residuals in the Kunia soil indicate that three years after the accidental spill, the main body of residuals still remained in the top 10-m layer of soils. Therefore, the DBCP detected in the water from the Kunia Well (about 300 m below the ground surface) is not likely a direct result of the DBCP spillage. A more detailed study revealed that the pesticide storage and mixing facility near the spill site is more likely the cause of the Kunia Well contamination (Liu et al. 1983).

CONCLUSIONS

Transport of chemical residuals in soil has been traditionally investigated by a physically based modeling approach. Usually, a physically based model consists of a set of partial differential equations, with auxiliary equations describing boundary and initial conditions. Relevant hydrodynamic mixing and reaction kinetics mechanisms are represented by model parameters. Practical application of a physically based model is often difficult because of the interrelated problems of identifying values of model parameters, of defining boundary and initial conditions, and of mathematical solution.

An alternative transport model can be formulated by following a system approach. In general, a system model formulated on the basis of the theory of hereditary processes is phenomenological in nature. It describes the overall behavior of hydrodynamic mixing and reaction kinetics mechanisms by response functions without specifying the intimate structure of these mechanisms. A linear system is described by a single impulse response function. Chemical residual distributions can be readily calculated by an integral equation that denotes the mathematical operation of convolution of chemical input function and impulse response function of the soil system.

In practical problems, the impulse response functions of a linear system can be determined by methods of system inversion, system parameterization, or physical parameterization. The full benefit of the system approach for modeling chemical residual transport in soil will be realized only by a conjunctive application of all three methods. In this study, only the method of physical parameterization was investigated. Although limited in scope, our study demonstrates the compatibility of the linear system modeling approach with the traditional,

physically-based modeling approach. It also demonstrates the computational superiority of the system approach, especially for the more complex two-component, two-layered soil system.

In solute transport in aggregated soils, soil-water content may be divided into two components: a mobile component of soil water in large pores and an immobile component of soil water in small pores. Successful simulation of solute transport in aggregated soils can be accomplished by a two-component multi-layered system model.

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APPENDIX CONTENTS

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APPENDIX A. ONE-DIMENSIONAL, ADVECTION-DISPERSION MODEL
FOR MASS TRANSPORT IN SOIL

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C*****
C
C THIS PROGRAM COMPUTES THE ANALYTICAL SOLUTION OF THE ONE-DIMENSIONAL
C CONVECTION-DISPERSION MASS TRANSPORT EQUATION. THE MODEL ALSO
C ALLOWS THE INVESTIGATION OF PESTICIDE RETENTION AND DECAY IN SOIL DUE
C TO ADSORPTION.
C*****
C
C *****MODEL PARAMETERS & VARIABLES & ARRAYS*****
C C0 INITIAL CONCENTRATION IN LIQUID
C D DISPERSION COEFFICIENT (SQ CM/DAY)
C V VELOCITY (CM/DAY)
C GAMMA SOURCE DECAY(VOLATILIZATION) CONSTANT (PER DAY)
C KD ADSORPTION COEFF (ML/(G*1.E - 6))
C PB DRY BLOCK SOIL DENSITY
C CITA VOLUMETRIC WATER CONTENT(CUBIC CM WATER/CUBIC CM SOIL)
C R RETARDATION FACTOR R =1. + PB*KD/CITA
C VR MODIFIED PERCOLATING VELOCITY (CM/DAY) VR = V/R
C DR MODIFIED DISPERSION COEFF (SQ CM/DAY) DR = D/R
C ARRAY C PESTICIDE CONCENTRATION IN SOLUTION (PPB)
C ARRAY CT TOTAL CONCENTRATION OF PESTICIDE (PPB)
C ARRAY PS PESTICIDE CONCENTRATION ADSORBED TO SOIL (PPB)
C ARRAY T0 TIME AFTER DBCP SPILL (DAY)
C ARRAY Z SOIL DEPTH (CM)
C ARRAY T COMPUTED TIME (DAY) T = T0 - 3.
C ARRAY X COMPUTED DEPTH (CM) X = Z - 5.
C*****
C
C *****DIFFERENTIAL EQUATION AND ITS SOLUTION*****
C
C (PB*KD/CITA +1.)*DT(C) = D*DDZ(C) - V*DZ(C)
C
C WITH BOUNDARY CONDITION C(0,T) = C0*EXP(-GAMMA*T)
C
C THE SOLUTION IS
C
C C(Z,T) = .5*C0*EXP((VR/(2.*DR))*Z - GAMMA*T)*
C (EXP(-SQRT(VR**2 - 4.*GAMMA*DR)*Z/(2.*DR))*
C ERFC(.5*Z/SQRT(DR*T) - SQRT((VR**2*.25/DR - GAMMA)*T)) +
C EXP(SQRT(VR**2 - 4.*GAMMA*DR)*Z/(2.*DR))*
C ERFC(.5*Z/SQRT(DR*T) + SQRT((VR**2*.25/DR - GAMMA)*T)))
C PS(Z,T) = PB*KD*C(Z,T)
C CT(Z,T) = PS(Z,T) + CITA*C(Z,T)
C*****
C
REAL T0(6)
REAL T(6),C(6), Z(21),CT(6),PS(21,6)
REAL KD
DATA Z/5.,50.,100.,150.,200.,250.,300.,350.,400.,450.,500.,
& 550.,600.,650.,700.,750.,800.,850.,900.,950.,1000./
DATA T0/5.,50.,100.,365.,730.,1095./
DATA PB,KD,CITA,V,D/1.8,0.2,.3,1.16,2.4/
WRITE*, 'INPUT C0,GAMMA'
READ*,C0,GAMMA
N = 6
WRITE(*,8)

```

```

WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
R = 1. + PB*KD/CITA
VR = V/R
DR = D/R
C NO APPRECIABLE RAINFALL RECORDED FOR KUNIA AREA AFTER SPILL EPISODE
C UNTIL APRIL 11, THUS SPILLED PESTICIDE WOULD REMAIN IN THE INITIAL ZONE FOR
C 3 DAYS BEFORE IT COULD MOVE DOWN
DO 10 I = 1,6
10 T(I) = T0(I) - 3.
C INITIAL PENETRATION IS ABOUT 5CM
DO 20 J = 1,21
9 X = Z(J) - 5.
DO 40 I = 1,6
C(I) = .5*C0*EXP(X*(VR*.5/DR) - GAMMA*T(I))*(EXP(-X*SQRT(VR*VR
& - 4.*GAMMA*DR)*.5/DR)
& *ERFC(X*.5/SQRT(DR*T(I)) - SQRT(T(I)*(VR*VR*.25/DR - GAMMA)))
& + EXP(X*SQRT(VR**2 - 4.*GAMMA*DR)*.5/DR)*ERFC(X*.5/SQRT(DR*T(I))
& + SQRT(T(I)*(VR*VR*.25/DR - GAMMA))))
PS(J,I) = PB*KD*C(I)
40 CT(I) = CITA*R*C(I)
8 FORMAT(1X,'COMPUTED TOTAL DBCP CONCENTRATION IN TOP 1000 CM/'
& 1X,'OF SOIL AT KUNIA SPILL SITE')
1 FORMAT(50X,'TIME (DAYS)')
2 FORMAT(8X,6(5X,F6.1))
3 FORMAT(7X,'|',6('-----|'),'T'/7X,'|'/)
WRITE(*,4) Z(J),(CT(I),I = 1,6)
4 FORMAT(F8.1,6(1X,F10.3)/7X,'|'/)
20 CONTINUE
WRITE(*,7)
7 FORMAT(7X,'|'/7X,'X'/1X,'DISTANCE (CM)')
WRITE(*,48)
48 FORMAT(7X,'COMPUTED DBCP CONCENTRATION IN SOIL SOLUTION')
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
DO 49 J = 1,21
WRITE(*,4) Z(J),(C(J,I),I = 1,6)
49 CONTINUE
WRITE(*,7)
WRITE(*,58)
58 FORMAT(7X,'COMPUTED DBCP CONCENTRATION ADSORBED TO SOIL')
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
DO 59 J = 1,21
WRITE(*,4) Z(J),(PS(J,I),I = 1,6)
59 CONTINUE
WRITE(*,7)
END

```

APPENDIX B. MASS TRANSPORT SYSTEM MODEL FOR TWO-COMPONENT,
TWO-LAYER SOIL UNIT

```

C*****
C
C THIS PROGRAM SOLVES THE INTEGRAL EQUATION OF A MASS TRANSPORT MODEL
C BY A SYSTEM APPROACH FOR A TWO-COMPONENT, TWO-LAYER SOIL UNIT. THE
C MODEL ALSO ALLOWS THE INVESTIGATION OF PESTICIDE RETENTION IN SOIL DUE
C TO ADSORPTION AND VOLATILIZATION. THE PROGRAM USES THE IMSL SUBROUTINE
C FLINV TO CONDUCT THE LAPLACE INVERSION.
C
C*****
C
C *****MODEL PARAMETERS & ARRAYS*****
C C0 INITIAL CONCENTRATION IN LIQUID IN MOBILE PHASE (PPB)
C D DISPERSION COEFFICIENT (SQ CM/DAY)
C V VELOCITY (CM/DAY)
C VM VELOCITY IN MOBILE PHASE VM = V/FITAM (CM/DAY)
C GAMMA SOURCE DECAY (VOLATILIZATION) CONSTANT (PER DAY)
C KD ADSORPTION COEFF (ML/G*1.E - 6)
C PB DRY BLOCK SOIL DENSITY
C FITAM MOBILE PHASE VOLUME FRACTION FITAM = CITAM/CITA
C CITA TOTAL VOLUMETRIC WATER CONTENT (CUBIC CM WATER/CUBIC CM
C SOIL)
C CITAM VOLUMETRIC WATER CONTENT IN MOBILE PHASE
C F MASS FRACTION OF SOLID PHASE SORBING FROM/IN COMPONENT 1
C R TOTAL RETARDATION FACTOR R = 1. + PB*KD/CITA
C R1 RETARDATION FACTOR IN MOBILE PHASE R1 = 1. + F*PB*KD/CITAM
C P PECLET NUMBER P = VM*AL/D
C W W = RAFA*AL/(CITA*V)
C RAFA MASS TRANSFER COEFF BETWEEN COMPONENTS (PER DAY)
C B B = FITAM*R1/R
C AL CHARACTERISTIC DEPTH WHERE WE DIVIDE TWO LAYERS
C BETA BETA = CITA2/CITA
C FITAM2,CITAM2,CITA2,F2,R2,R12,P2,W2,B2,V2,VM2,KD2 ARE FITAM,CITAM,
C CITA,F,R,R1,P,W,B,V,VM,KD IN SECOND SOIL LAYER
C ARRAY CR1 SOLUTE CONCENTRATION IN SOLUTION IN MOBILE PHASE (PPB)
C ARRAY CR2 SOLUTE CONCENTRATION IN SOLUTION IN IMMOBILE PHASE (PPB)
C ARRAY PS DBCP CONCENTRATION ADSORBED TO SOIL (PPB)
C ARRAY CT TOTAL CONCENTRATION OF PESTICIDE (PPB)
C ARRAY T0 TIME AFTER DBCP SPILL (DAY)
C ARRAY Z0 SOIL DEPTH (CM)
C ARRAY T DIMENSIONLESS TIME T = (T0 - 3.)*V/AL
C ARRAY X DIMENSIONLESS DEPTH X = Z0/AL
C TWO DIMENSIONAL ARRAY DR1,DR2 USED TO CONTAIN COMPUTED CR1,CR2
C COMPLEX FUNCTION C1 LAPLACE TRANSFORM OF CR1 AS TO T
C COMPLEX FUNCTION C2 LAPLACE TRANSFORM OF CR2 AS TO T
C
C*****
C
C *****DERIVATION AND SOLUTION OF MODEL *****
C DIFFERENTIAL EQUATIONS:
C (PB*KD*F + CITAM)*DT(CR1) + (PB*KD*(1. - F) + CITA - CITAM)*DT(CR2)
C = D*CITAM*DDZ(CR1) - VM*CITAM*DZ(CR1) (1)
C (PB*KD*(1. - F) + CITA - CITAM)*DT(CR2) = RAFA*(CR1 - CR2) (2)
C EQUATIONS CAN ALSO BE WRITTEN AS
C B*R*DT(CR1) + (1. - B)*R*DT(CR2) = 1/P*DDX(CR1) - DX(CR1) IF X < 1 (3)
C (1. - B)*R*DT(CR2) = W*(CR1 - CR2) IF X < 1 (4)
C BETA*(B2*R2*DT(CR1) + (1 - B2)*R2*DT(CR2)) = 1/P2*DDX(CR1)

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C          -DX(CR1  IF X > 1                                (5)
C          BETA*(1 - B2)*R2*DT(CR2) = W2*(CR1 - CR2)    F X > 1    (6)
C          WITH PARAMETERS AS SHOWN ABOVE
C          WITH BOUNDARY CONDITION CR1(X,T) = C0*EXP(-GAMMA*T)
C          DO LAPLACE TRANSFORM OF (3),(4),(5),(6) AS TO T
C          IF X < 1(Z0 < AL) IN FIRST SOIL LAYER
C          WE HAVE
C          CR1(X,S) = C0(S)*EXP((X - .1)*(P/2 - .5*SQRT(P**2 + 4.*B*R*P*S0)))
C                   = C0/(GAMMA + S)*EXP((X - .1)*(P/2 - .5*SQRT(P**2 + 4.*B*R*P*S0)))
C          WHERE
C          S0 = S*(1. + ((1. - B)*W/B)/((1. - B)*R*S + W))
C          CR2(X,S) = W/((1. - B)*R*S + W)*CR1(X,S)
C          IF X > 1 (Z0 > AL) IN THE SECOND SOIL LAYER
C          INITIAL PENETRATION IS 5 CM, X = .1
C          WE HAVE
C          CR1(X,S) = C0/(GAMMA + S)*EXP{.9*[P/2 - .5*SQRT(P**2
C                   + 4.*B*R*P*S0)] + (X - 1)*[P/2 - .5*SQRT(P2**2 + 4.*B2*R2*P2*BETA*S1)]}
C          WHERE
C          S0 = S*(1. + ((1. - B)*W/B)/((1. - B)*R*S + W))
C          S1 = S*(1. + ((1. - B2)*W2/B2)/((1. - B2)*R2*BETA*S + W2))
C          CR2(Z,S) = W2/((1. - B2)*R2*BETA*S + W2)*CR1(Z,S)
C          PARAMETERS P,B,R,W,V,P2,B2,R2,W2,V2 AS SHOWN ABOVE
C          USE IMSL SUBROUTINE FLINV TO DO THE INVERSE LAPLACE TRANSFORM
C          TOTAL DBCP CONCENTRATION:
C          CT(X,T) = CITA*(B*R*CR1(X,T) + (1 - B)*R*CR2(X,T)  IF X < 1    (7)
C          CT(X,T) = CITA2*(B2*R2*CR1(X,T) + (1 - B2)*R2*CR2(X,T))  F X > 1    (8)
C*****
C
C          *****IMSL ROUTINE NAMEFLINV*****
C          PURPOSE  INVERSE LAPLACE TRANSFORM OF A USER SUPPLIED COMPLEX
C          FUNCTION
C          USAGE    - CALL FLINV(F,N,T,ALPHA,NSIG,KMAX,FINV,IER)
C          ARGUMENTS F  - USER SUPPLIED COMPLEX FUNCTION TO BE
C                   - INVERSED F(S)
C                   N  - NUMBER OF POINTS AT WHICH INVERSE LAPLACE
C                   - TRANSFORM IS TO BE CALCULATED
C                   T  - VECTOR OF LENGTH N CONTAINS POINTS AT WHICH
C                   - INVERSE LAPLACE TRANSFORM IS TO BE CALCULATED
C                   ALPHA - MAXIMUM OF REAL PARTS OF SINGULARITIES OF F(S),
C                   - OR AN ESTIMATED VALUE GREATER THAN THIS MAXIMUM
C                   NSIG - INTEGER VALUE SPECIFYING NUMBER OF SIGNIFICANT
C                   - DIGITS DESIRED IN OUTPUT VECTOR FINV (INPUT)
C                   KMAX - ALGORITHM CAN USE 3*KMAX FUNCTION EVALUATIONS
C                   - FOR EACH T(I) (INPUT)
C                   FINV - OUTPUT VECTOR OF LENGTH N. FINV CONTAINS VALUE
C                   - OF INVERSE LAPLACE TRANSFORM OF USER-SUPPLIED
C                   - FUNCTION AT T(I).
C                   IER  - ERROR PARAMETER (OUTPUT)
C                   IER = 129 INDICATES THAT ALGORITHM COULD NOT
C                   - ACHIEVE ACCURACY REQUESTED WITHIN KMAX
C                   - FUNCTION EVALUATIONS FOR SOME T(I)
C                   IER = 130 INDICATES THAT OVERFLOW WOULD HAVE
C                   - OCCURRED FOR A PARTICULAR VALUE OF T
C*****

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```

REAL T(6),ALPHA,CR1(6),CR2(6),Z0(21),CT(6)
REAL T0(6),KD,KD2
REAL DR1(21,6),DR2(21,6),PS(21,6)
COMPLEX C1,C2
EXTERNAL C1,C2
COMMON AL,P,B,R,W,X,IZ,V,P2,B2,R2,W2,V2,C0,GAMMA,BETA
& DATA Z0/5.,50.,100.,150.,200.,250.,300.,350.,400.,450.,500.,
& 550.,600.,650.,700.,750.,800.,850.,900.,950.,1000./
DATA T0/5.,50.,100.,365.,730.,1095./
& DATA F,PB,KD,FITAM,CITA,RAFA, D
/ .75,1.8,1.94, .75, .3, .1,2.4/
DATA KD2,CITA2/.02, .3/
DATA FITAM2,F2/.5, .5/
CITAM = FITAM*CITA
CITAM2 = FITAM2*CITA2
WRITE*, 'V C0 GAMMA'
READ*, V,C0,GAMMA
AL = 50.
VM = V/FITAM
WRITE(*,9) F,PB,KD,KD2,CITAM,CITA,C0,GAMMA,RAFA,AL,VM,V,D
9 FORMAT(////6X,'F =',F5.2,'PB =',F5.2,'KD =',F7.4,'KD2 =',F7.4/
& 6X,'CITAM =',F7.3,'CITA =',F7.3,'C0 =',F7.1,'GAMMA =',F8.4/
& 6X,'RAFA =',F7.3,'AL =',F7.3,'VM =',F7.3,'V =',F7.3,'D =',F7.3)
WRITE(*,11)CITA2,FITAM2,F2
11 FORMAT(6X,'CITA2 =',F5.2,'FITAM2 =',F5.2,'F2 =',F5.2)
C CHANGE GAMMA TO DIMENSIONLESS GAMMA
GAMMA = GAMMA*AL/V
C SPILLED PESTICIDES WOULD REMAIN IN INITIAL ZONE FOR 3 DAYS, BECAUSE NO
C APPRECIABLE RAINFALL WAS RECORDED FOR THE KUNIA AREA AFTER SPILL.
C DIMENSIONLESS TIME
DO 10 I = 1,6
10 T(I) = (T0(I) - 3.)*V/AL
N = 6
ALPHA = 0.E0
NSIG = 4
KMAX = 200
WRITE(*,8)
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
C CALCULATING PARAMETERS
R1 = (1. + F*PB*KD/CITAM)
R = (1. + PB*KD/CITA)
P = VM*AL/D
B = FITAM*R1/R
W = RAFA*AL/(V*CITA)
R2 = (1. + PB*KD2/CITA2)
R12 = 1. + F2*PB*KD2/CITAM2
B2 = FITAM2*R12/R2
V2 = V*CITA/CITA2
VM2 = V2/FITAM2
P2 = VM2*AL/D
W2 = RAFA*AL/(V2*CITA2)
C DIMENSIONLESS SOIL DEPTH
DO 20 J = 1,21
X = Z0(J)/AL
IF(Z0(J).LE.AL) THEN
IZ = 1

```

```

ELSE
Z = 2
ENDIF
CALL FLINV(C1,N,T,ALPHA,NSIG,KMAX,CR1,IER)
CALL FLINV(C2,N,T,ALPHA,NSIG,KMAX,CR2,IER)
DO 40 I = 1,6
IF(IZ.EQ.1) THEN
CT(I) = C0*(B*R*CITA*CR1(I) + (1. - B)*R*CITA*CR2(I))
PS(J,I) = C0*PB*KD*F*CR1(I) + C0*PB*KD*(1. - F)*CR2(I)
ELSE
CT(I) = C0*(B2*R2*CITA2*CR1(I) + (1. - B2)*R2*CITA2*CR2(I))
PS(J,I) = C0*PB*KD2*F2*CR1(I) + C0*PB*KD2*(1. - F2)*CR2(I)
ENDIF
DR1(J,I) = CR1(I)*C0
DR2(J,I) = CR2(I)*C0
40 CONTINUE
8 FORMAT(6X,'COMPUTED TOTAL DBCP CONCENTRATION AT TOP 1000 CM/'
& 6X,'OF SOIL AT KUNIA SPILL SITE')
1 FORMAT(50X,'TIME (DAYS)')
2 FORMAT(10X,6(5X,F6.1))
3 FORMAT(9X,'|',6('-----|'),'T')
WRITE(*,4) Z0(J),(CT(I),I = 1,6)
4 FORMAT(F10.1,6(1X,F10.3))
20 CONTINUE
WRITE(*,7)
7 FORMAT(10X,'|',/9X,'X'/9X,'DISTANCE (CM)')
WRITE(*,5)
5 FORMAT(/6X,'COMPUTED DBCP CONCENTRATION IN MOBILE PHASE')
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
DO 501 K = 1,21
WRITE(*,4) Z0(K),(DR1(K,I),I = 1,6)
501 CONTINUE
WRITE(*,7)
WRITE(*,6)
6 FORMAT(/6X,'COMPUTED DBCP CONCENTRATION IN IMMOBILE PHASE')
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
DO 502 J = 1,21
WRITE(*,4) Z0(J),(DR2(J,I),I = 1,6)
502 CONTINUE
WRITE(*,7)
WRITE(*,16)
16 FORMAT(6X,'COMPUTED DBCP CONCENTRATION ADSORBED TO SOIL')
WRITE(*,1)
WRITE(*,2) T0
WRITE(*,3)
DO 503 J = 1,21
WRITE(*,4) Z0(J),(PS(J,I),I = 1,6)
503 CONTINUE
WRITE(*,7)
END

```

C*****

```

COMPLEX FUNCTION C1(S)
COMPLEX S
COMMON AL,P,B,R,W,X,IZ,V,P2,B2,R2,W2,V2,C0,GAMMA,BETA
IF (IZ.EQ.1) THEN
C INITIAL PENETRATION IS 5 CM (X = .1), WITH (AL = 50 CM), X = .1
& C1 = EXP((X - .1)*(.5*P - .5*SQRT(P*P + 4.*P*(B*R*S + (1. - B)*R
& *S*W/((1. - B)*R*S + W))))/(S + GAMMA)
& ELSE
& C1 = EXP(.9*(.5*P - .5*SQRT(P*P + 4.*P*(B*R*S + (1. - B)*R
& *S*W/((1. - B)*R*S + W))))/(S + GAMMA)*EXP((X - 1.)*(.5*P2 - .5*SQRT
& (P2*P2 + 4.*P2*(B2*R2*BETA*S + (1. - B2)*BETA*R2*S*W2/((1. - B2)*BETA*R2*S
& + W2))))))
& ENDIF
RETURN
END

```

C*****

```

COMPLEX FUNCTION C2(S)
COMPLEX S
COMMON AL,P,B,R,W,X,IZ,V,P2,B2,R2,W2,V2,C0,GAMMA,BETA
IF (IZ.EQ.1) THEN
C INITIAL PENETRATION IS 5 CM (X = .1)
& C2 = EXP((X - .1)*(.5*P - .5*SQRT(P*P + 4.*P*(B*R*S + (1. - B)*R
& *S*W/((1. - B)*R*S + W))))*W/
& ((1. - B)*R*S + W)/(S + GAMMA)
& ELSE
& C2 = EXP(.9*(.5*P - .5*SQRT(P*P + 4.*P*(B*R*S + (1. - B)*R
& *S*W/((1. - B)*R*S + W))))*W2/((1. - B2)*R2*BETA*S + W2)/(S + GAMMA)
& *EXP((X - 1.)*(.5*P2 - .5*SQRT(P2*P2 + 4.*P2*(B2*R2*BETA*S + (1. - B2)
& *R2*BETA*S*W2/((1. - B2)*R2*BETA*S + W2))))))
& ENDIF
RETURN
END

```