

Behavior Assessment Model for Trace Organics in Soil: I. Model Description¹

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ABSTRACT

A mathematical model is introduced for describing transport and loss of soil-applied organic chemicals. The model assumes linear, equilibrium partitioning between vapor, liquid, and adsorbed chemical phases, net first order degradation, and chemical movement to the atmosphere by volatilization loss through a stagnant air boundary layer at the soil surface. From these assumptions and the assumption of steady state upward or downward water flow, an analytic solution is derived for chemical concentration and volatilization flux.

This model, which is intended to classify and screen organic chemicals for their relative susceptibility to different loss pathways (volatilization, leaching, degradation) in the soil and air, requires knowledge of the organic carbon partition coefficient (K_{oc}), Henry's constant (K_H), and net, first-order degradation rate coefficient or chemical half-life to use on a given chemical.

Illustration of the outputs available with the model is shown for two pesticides, lindane (γ -1,2,3,4,5,6-hexachlorocyclohexane) and 2,4-D [(2,4-dichlorophenoxy)acetic acid], which have widely differing chemical properties. Lindane, with a large K_{oc} , large K_H , and small degradation rate coefficient, is shown to be relatively immobile, persistent, and susceptible to volatilization. 2,4-D, with a small K_{oc} , small K_H , and large degradation rate coefficient, is mobile and degrades rapidly, but is only slightly susceptible to losses by volatilization.

Additional Index Words: pesticide, chemical movement, volatilization, diffusion, leaching.

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Beginning with DDT in the late 1960's, several established pesticides with effective weed or insect control were removed from the market because of undesirable

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environmental characteristics. Unfortunately, these undesirable characteristics (such as excessive mobility, persistence, or volatility) were determined or observed only after the chemical had been widely used. Because a certain amount of mobility and persistence is essential for proper management and performance of a pesticide, its pollution potential can only be minimized subject to its effectiveness for weed or insect control.

For this reason, it is clear that environmental screening tests are needed at the time of development of the chemical when screening for toxicity is being performed. It is equally clear that this screening procedure cannot involve excessive experimentation, because of the massive numbers of chemicals involved. Instead, what it needed is a model that is able to make predictions of behavior of one chemical relative to another from a standard set of easily obtainable chemical benchmark properties.

Ideally, the result of this screening procedure would be a classification of large numbers of chemicals into a smaller number of groups whose members display similar behavior. From these groups could be selected prototypes for more extensive experimentation under natural conditions.

Pesticide simulation models are not new. Lindstrom et al. (1968) proposed a mathematical model for describing leaching of pesticides through soil columns. Oddson et al. (1970) and Davidson and McDougal (1973) reported a theoretical leaching model for use with chemicals whose solid-liquid adsorption was linear, but for which the liquid and solid phases were not in equilibrium. Van Genuchten and coworkers, in a series of papers (Van Genuchten et al., 1974, 1977; Van Genuchten & Wierenga, 1976, 1977), described a model for predicting pesticide movement in soil, including effects of pore bypass and hysteresis in the adsorption isotherm, and validated the model in soil column experiments using 2,4,5-T herbicide. They also investigated the effect of nonequilibrium adsorption. Leistra, in a series of papers (Leistra, 1973, 1978, 1979), has devel-

oped simulation models for both liquid and vapor phase movement as a function of time for variable boundary conditions. Knisel (1980) has assembled (with the aid of a number of authors) a model (CREAMS) for evaluating the amounts of pesticide in surface runoff.

Volatilization models have also been developed. Mayer et al. (1974) compared five different models, employing various upper-boundary conditions for predicting volatilization of chemicals from soil. Farmer et al. (1980) developed a soil cover model for hexachlorobenzene, which demonstrated the effectiveness of deep placement to prevent volatilization. Jury et al. (1980) proposed and validated a model for predicting volatilization losses of triallate, with and without accompanying soil water evaporation.

The above models, for the most part, were intended to simulate specific circumstances, either of leaching or of volatilization. In this paper, and those to follow, we will propose and apply a general model that includes the effects of volatilization, leaching, and degradation to describe the major loss pathways of soil-applied organic chemicals as a function of specific environmental variables and soil conditions. In this way, the behavior of one chemical relative to another in a standard scenario will reveal the susceptibility of the tested chemicals to various loss or displacement pathways in soil. Thus, the model simulations are not intended to predict a chemical's concentration distribution in a field, but merely to group chemicals according to their behavior in the environmental screening tests. Although the model will be primarily used on pesticides in this series of papers, it is applicable as well to other trace organics that may be of environmental concern. This first paper will describe the model and illustrate its output using the chemical and physical characteristics of lindane (γ -1,2,3,4,5,6-hexachlorocyclohexane) and 2,4-D [(2,4-dichlorophenoxy)acetic acid]. Later papers in this series will develop a classification scheme for the susceptibility of chemicals to leaching, volatilization, or degradation; will examine the experimental evidence in support of the model assumptions and predictions; and will apply the model to screen a large number of organic chemicals.

BENCHMARK PROPERTIES NEEDED TO PREDICT PESTICIDE LOSS FROM SOILS

In this section, we will attempt to define a minimum set of chemical and physical characteristics for a given pesticide, which must be known in order to make a reliable assessment of the extent of loss through volatilization, leaching, and/or degradation in soil. The emphasis will be on developing criteria for determining relative behavior of different pesticides under prototype conditions.

Phase Partitioning Coefficients

A pesticide may reside in either the vapor, liquid, or adsorbed phase, but it is essential to know how a given quantity of applied chemical will partition between these three phases in the soil in order to determine its mobility in soil.

The adsorbed-liquid partitioning is expressed through an adsorption isotherm. At low concentrations, the shape of this isotherm may frequently be approximated by a straight line (Karickhoff et al., 1979; Karickhoff, 1981), giving rise to the simple, linear relationship in Eq. [1].

$$C_S = K_D C_L, \quad [1]$$

where C_S is adsorbed concentration (g/kg soil), C_L is solution concentration (g/m³ soil solution), and K_D (m³/kg) is the slope of the adsorption isotherm of the distribution coefficient. Since this distribution coefficient (for nonionic pesticides, at least) primarily represents adsorption to organic matter, variability between soils may be reduced to an extent by defining an organic carbon distribution coefficient,

$$K_{oc} = K_D / f_{oc}, \quad [2]$$

where f_{oc} is the fraction of organic C in the soil. This standardization greatly decreases the coefficient of variability of the adsorption coefficient for a given pesticide in different soils (Hamaker & Thompson, 1972; Rao & Davidson, 1980).

When measured adsorption values are not available, reasonably good correlation has been found between K_{oc} and the octanol-water partition coefficient, K_{ow} , or between K_{oc} and solubility and melting point (Karickhoff, 1981). For example, Rao and Davidson (1980) developed the regression equation (Eq. [3]) using published data for a number of pesticides.

$$\log(K_{oc}/1000) = 1.029 \log(K_{ow}/1000) - 0.18; \quad [3]$$

$$r^2 = 0.91$$

where the factor of 1000 is needed because K is expressed in SI units (m³/kg) and their regression used (mL/g) for the units of K . The limitations of the above partitioning approach are discussed in a recent review by Mingelgrin and Gerstl (1983).

The liquid-vapor partition, as mentioned above, is generally represented through Henry's Law,

$$C_G = K_H C_L, \quad [4]$$

where C_G is concentration of pesticide in the vapor phase (g/m³ soil air) and K_H is Henry's Law constant, which in this system of units is dimensionless. Because studies have shown (Spencer & Cliath, 1970) that this relationship persists to saturation in many circumstances, the Henry's Law constant may be calculated as the ratio of saturated vapor density C_G^* (g/m³) to pesticide solubility C_L^* (g/m³):

$$K_H = C_G^* / C_L^*. \quad [5]$$

Degradation Coefficients

Because the degradation rate constant or half-life is a direct assessment of the persistence of the pesticide, it must also be classed as an essential parameter for evaluation. In the vast majority of studies, a net, first-order degradation rate is assumed for all degradative processes in all phases, and the rate constant, μ (per day) is measured by the rate equation

$$M(t) = M(0) \exp(-\mu t), \quad [6]$$

where $M(t)$ is the quantity of pesticide remaining at time t . The half-life, $T_{1/2}$, is related to the rate constant, μ , by $T_{1/2} = 0.693/\mu$.

Unfortunately, measurements of μ vary enormously between field and laboratory data because "degradation losses" generally include other unmeasured pathways of loss. Furthermore, temperature, water content, and microbial population can influence these processes significantly. Thus, this parameter is both extremely important and extremely difficult to assess. For example, Hamaker (1972) reports a half-life for simazine of 105 d ($\pm 34\%$), which contrasts with values of 75

* Refers to saturation values.

d (lab) and 64 d (field) given by Rao and Davidson (1980) and with 55 d ($\pm 63\%$) given by Nash (1980).

Diffusion Coefficients

Other than mass flow in the soil-water phase, the two dominant transport processes for pesticides in soil are vapor and liquid diffusion. The soil-gas diffusion coefficient, D_G , is usually equated to the air-gas diffusion coefficient, D_G^{air} , multiplied by a tortuosity factor to account for the reduced flow area and increased path length of diffusing gas molecules in soil (Nielsen et al., 1972). This tortuosity factor is a function of volumetric air content, α , and of soil geometry, and has been described using a variety of models (Rose, 1972). One such model that has proven useful for describing pesticide soil diffusion coefficients is the Millington-Quirk model (Shearer et al., 1973; Farmer et al., 1972). With this model, we obtain for the soil-gas diffusion coefficient:

$$D_G = (\alpha^{10/3}/\phi^2) D_G^{air}, \quad [7]$$

where ϕ is the soil porosity.

Because the Millington-Quirk tortuosity formula does not have any calibration constants, the only pesticide property that needs to be measured is the air-gas diffusion coefficient. However, by examining the range of existing values for intermediate molecular weight organic compounds (Boynton & Brattain, 1929), as well as by using the Fuller correlation (Liley & Gambill, 1973), one may show that the air-gas diffusion coefficient of different pesticides varies only slightly at a given temperature. For this reason, we consider that the representative value $D_G^{air} = 0.43 \text{ m}^2/\text{d}$ from the data of Boynton and Brattain (1929) is adequate for most pesticides and need not be measured in every case.

Similarly, the soil liquid diffusion coefficient D_L is set equal to the water-liquid diffusion coefficient D_L^{water} multiplied by the appropriate form of the Millington-Quirk tortuosity model.

$$D_L = (\theta^{10/3}/\phi^2) D_L^{water}, \quad [8]$$

where θ (volumetric water content) $= \phi - \alpha$. Although few, if any, water-liquid diffusion coefficient measurements have been made on pesticides, other similar molecular weight organic compounds seem to differ only slightly in value (Bruins, 1929). From the compilation of Bruins, we chose an average $D_L^{water} = 4.3 \times 10^{-5} \text{ m}^2/\text{d}$ as a representative value for all pesticides.

Influence of Hydrodynamic Dispersion

Many modelers of chemical transport in soil include a dispersion term in the flux equation to account for solute spreading due to water velocity variations. At low average water fluxes in uniform soil, this term is relatively unimportant, but it becomes dominant over the diffusion term at high water fluxes or in structured soil where substantial variation in water velocities exists. Because we will be using our model in uniform, idealized scenarios, the influence of spatially variable water velocities on transport is not part of the screening tests, and we will not be including a dispersion coefficient. The relative influence of dispersion on transport should be similar to that of diffusion between different chemicals, unless large structural voids are present.

In summary, among the primary properties discussed above, it is essential to measure the organic C partition coefficient, the saturated vapor density, the solubility, and the degradation half-life for each chemical. As we mentioned above, the two diffusion coefficients may be estimated relatively accurately from known information and need not be measured in each case.

There are a number of soil properties that will influence pesticide movement and loss. However, to a great extent, these properties may be standardized in assessing behavior, and the movement along various pathways of one pesticide relative to another may serve as an index of relative pollution hazard.

THEORY

The screening model introduced below is based on a number of simplifying assumptions. Our purpose in using this model is not to simulate chemical transport in a given field situation, but rather to estimate how and where a pesticide will move under a given set of imposed circumstances, particularly by describing the behavior of one chemical relative to another in an identical setting. In an attempt to be general (but at the same time to allow an analytic solution) we have chosen the following scenario for our pesticide screening model:

- 1) uniform soil properties consisting of a constant water content, θ ; bulk density, ρ_b ; porosity, ϕ ; liquid water flux, J_w (either upward, downward, or 0); and a constant organic C fraction, f_{oc} ,
- 2) linear, equilibrium adsorption isotherm so that Eq. [1] is valid,
- 3) linear, equilibrium liquid-vapor partition (Henry's Law), Eq. [4],
- 4) uniform initial incorporation of pesticide at time $t = 0$ between the surface and depth L , and
- 5) loss of pesticide and water to the atmosphere limited by gaseous diffusion through a stagnant air boundary layer above which the pesticide has zero concentration and the water is at 50% relative humidity.

The general transport theory will be derived below and simplified using these assumptions.

Mass Balance

In a one-dimensional, homogeneous porous medium, the mass conservation equation for a single pesticide species undergoing first-order decay may be written as:

$$\partial C_T / \partial t + \partial J_S / \partial Z + \mu C_T = 0, \quad [9]$$

where C_T = mass of solute per soil volume (g/m^3), J_S = solute mass flow per soil area per time ($\text{g}/\text{m}^2/\text{day}$), μ = net degradation rate (per day), t is time (day), and Z is soil depth (m).

Flux Equation

The mass flux may be written as (ignoring adsorbed-phase transport and hydrodynamic dispersion):

$$J_S = -D_G (\partial C_G / \partial Z) - D_L (\partial C_L / \partial Z) + J_w C_L, \quad [10]$$

where the first term represents gaseous diffusion, the second term describes liquid diffusion, and the third term describes convection of solute by mass flow of soil solution; D_G and D_L may be related to their values in pure air and water, respectively, through Eq. [7] and [8].

Concentration

Total solute concentration is made up of contributions from each phase, as expressed in Eq. [11].

$$C_T = \rho_b C_S + \theta C_L + \alpha C_G \quad [11]$$

Equations [9], [10], and [11] may be combined to form a second-order differential equation. However, two independent relations between C_S , C_L , and C_G are needed to produce a complete description of the transport and interaction between

phases. Using the linear, equilibrium approximations in Eq. [1] and [4], however, allows us to rewrite Eq. [9] and [10] in terms of one of the variables alone. Thus, Eq. [11] may be written as:

$$C_T = R_S C_S = R_L C_L = R_G C_G, \quad [12]$$

where

$$R_S = \rho_b + \theta/K_D + aK_H/K_D, \quad [13]$$

$$R_L = \rho_b K_D + \theta + aK_H, \text{ and} \quad [14]$$

$$R_G = \rho_b K_D/K_H + \theta/K_H + a \quad [15]$$

are the partition coefficients for the solid, liquid, and gaseous phases, respectively, which give the ratio of the total concentration C_T to the concentration in each representative phase.

Equations [12] through [15] allow us to rewrite Eq. [9] and [10] in terms of the total concentration, leaving us with:

$$J_S = -D_E(\partial C_T/\partial Z) + V_E C_T \text{ and} \quad [16]$$

$$\partial C_T/\partial T = D_E(\partial^2 C_T/\partial Z^2) - V_E(\partial C_T/\partial Z) - \mu C_T, \quad [17]$$

where D_E is the effective diffusion coefficient given by

$$D_E = (D_G/R_G) + (D_L/R_L) = (K_H D_G + D_L)/R_L, \quad [18]$$

and V_E is the effective solute convection velocity given by

$$V_E = J_w/R_L. \quad [19]$$

We could just as easily have written Eq. [9] and [10] in terms of any one of the three phases rather than the total concentration. The advantage of this form is that it automatically applies when, for example, only liquid flow is present, or only gaseous flow is present, and that it directly predicts total concentrations and losses. As pointed out above, the degradation rate coefficient may actually represent unequal contributions from each phase, weighted by the partition coefficients.

Prototype Screening Simulations

In a typical field situation, some pesticides are applied to a soil layer (surface or incorporated) and are subsequently influenced by leaching, volatilization, water evaporation, or degradation. The extent to which a particular compound is affected by a given process is a useful environmental as well as managerial index for classifying pesticides into categories. As mentioned above, we propose the following scenario as such a screening tool:

- 1) uniform incorporation of a quantity M (g/m^2) of chemical to a depth L (cm) below the surface,
- 2) volatilization through a stagnant air boundary layer of thickness, d , at the soil surface,
- 3) convection by a steady water flux $J_w = \pm J$ or 0, and
- 4) infinite depth of uniform soil below the depth of incorporation.

This scenario is idealized but sufficiently flexible to allow a variety of classifications to be made from a given series of calculations. The initial and boundary conditions appropriate to this scenario follow.

Boundary Conditions

INITIAL CONDITION

$$\begin{aligned} C_T(Z, 0) &= C_0 & \text{if } 0 < Z < L \\ C_T(Z, 0) &= 0 & \text{if } Z > L, \end{aligned} \quad [20]$$

where C_0 is the uniform initial concentration.

UPPER BOUNDARY CONDITION

$$J_S(0, t) = -hC_G(0, t), \quad [21]$$

where $h = D_G^{air}/d$, and is the transport coefficient across the stagnant air boundary layer of thickness d . This transport coefficient is actually a diffusion coefficient divided by a length; $C_G(0, t)$ is the gas concentration at the soil surface below the boundary layer. By assumption, the gas concentration at the top of the boundary layer, a height d above the surface, is zero. Thus, Eq. [21] is Fick's Law for the gas flux across the air layer. We may express Eq. [21] in terms of the total concentration using Eq. [16] and the partition coefficient R_G in Eq. [12].

$$-D_E \partial C_T/\partial Z + V_E C_T = -H_E C_T, \quad \text{at } Z = 0 \quad [22]$$

where $H_E = h/R_G$.

LOWER BOUNDARY CONDITION

$$C_T(\infty, t) = 0 \quad [23]$$

Solutions to Equations

If we neglect the possibility of chemical precipitation, we may solve Eq. [17], [20], [22], and [23] analytically to give

$$\begin{aligned} C_T(Z, t) &= \frac{1}{2} C_0 \exp(-\mu t) \\ &\left(\left\{ \operatorname{erfc} \left[\frac{(Z-L-V_E t)}{\sqrt{4D_E t}} \right] - \operatorname{erfc} \left[\frac{(Z-V_E t)}{\sqrt{4D_E t}} \right] \right\} \right. \\ &\quad \left. + (1 + V_E H_E) \exp(V_E Z/D_E) \right. \\ &\quad \left. \left\{ \operatorname{erfc} \left[\frac{(Z+L+V_E t)}{\sqrt{4D_E t}} \right] - \operatorname{erfc} \left[\frac{(Z+V_E t)}{\sqrt{4D_E t}} \right] \right\} \right. \\ &\quad \left. + (2 + V_E/H_E) \exp\{[H_E(H_E + V_E)t + (H_E + V_E)Z]/D_E\} \right. \\ &\quad \left. \left[\operatorname{erfc} \left[\frac{(Z+(2H_E + V_E t))}{\sqrt{4D_E t}} \right] - \exp(H_E L/D_E) \right. \right. \\ &\quad \left. \left. \operatorname{erfc} \left[\frac{[Z+L+(2H_E + V_E)t]}{\sqrt{4D_E t}} \right] \right] \right) \quad [24] \end{aligned}$$

Using Eq. [16], [22], and [24], we may write the volatilization flux at the surface as

$$\begin{aligned} J_S(0, t) &= \frac{1}{2} C_0 \exp(-\mu t) \\ &\left[V_E \left\{ \operatorname{erfc} \left(\frac{V_E t}{\sqrt{4D_E t}} \right) - \operatorname{erfc} \left[\frac{(L+V_E t)}{\sqrt{4D_E t}} \right] \right\} \right. \\ &\quad \left. + (2H_E + V_E) \exp[H_E(H_E + V_E)t/D_E] \right. \\ &\quad \left. \left\{ \exp(H_E L/D_E) \operatorname{erfc} \left[\frac{(L+(2H_E + V_E)t)}{\sqrt{4D_E t}} \right] \right. \right. \\ &\quad \left. \left. - \operatorname{erfc} \left[\frac{(2H_E + V_E)t}{\sqrt{4D_E t}} \right] \right\} \right], \quad [25] \end{aligned}$$

Table 1—Common properties assumed in calculations with lindane and 2,4-D.

Variable	Property	Value
D_G^{air}	Air diffusion coefficient	0.43 m ² /d
D_L^{water}	Water diffusion coefficient	4.3 × 10 ⁻³ m ² /d
ϕ	Porosity	0.5
ρ_b	Bulk density	1.350 (kg/m ³)
RH	Atmospheric relative humidity	0.5 (50%)
T	Temperature	25°C
f_{oc}	Organic carbon fraction	0.0125, 0.0250
θ	Water content	0.30 (m ³ /m ³)
M	Amount of pesticide applied	0.1 g/m ² (1 kg/ha)
L	Depth of incorporation	1, 10 (cm)
E	Water evaporation rate	0, 2.5, 5.0 × 10 ⁻³ (m/d)
J	Leaching rate	5 × 10 ⁻³ (m/d)

where $erfc(x)$ is the complementary error function. Other expressions may be written down, e.g., pesticide flux at other depths $J_s(Z, t)$, but are omitted here for brevity.

Boundary Layer Model

By assumption, both evaporation rate, E , and pesticide volatilization flux, $J_s(o)$, are limited by diffusion through the stagnant air layer of thickness d above the soil surface. Therefore, since we specify evaporation rate, we must select a consistent boundary layer thickness. To make the appropriate selection, one writes the water and pesticide diffusion equations across the air layer at the soil surface.

Water Vapor Transport

$$E = D_{wv}^{air} [q_{wv}(0) - q_{wv}(d)] / q_{wL} d \quad [26]$$

Pesticide Vapor Transport

$$J_s = D_G^{air} [C_G(0) - C_G(d)] / d, \quad [27]$$

where q_{wv} (g/m³) is water vapor density, q_{wL} (g/m³) is liquid water density, and D_{wv}^{air} is the binary diffusion coefficient of water vapor in air (≈ 2 m²/d; Boynton & Brattain, 1929). If we further assume that q_{wv} is saturated at the surface ($q_{wv} = q_{wv}^*$), that $C_G(d) = 0$, and that our steady state evaporation rate is equal to one-half of a typical evaporation rate (which would be negligible at night), we arrive at the final relation for d :

$$d = D_{wv}^{air} q_{wv}^* (1 - RH) / 2E q_{wL}, \quad [28]$$

where RH = atmospheric relative humidity. Equation [28] was used in all calculations that follow, where upward water

flux was nonzero. In calculations where $E = 0$ (i.e., $RH = 1$), d was given a specified value of 4.75×10^{-3} m. This value of d is obtained with $E = 2.5 \times 10^{-3}$ m/d (2.5 mm/d), and $RH = 0.5$ in Eq. [28].

ILLUSTRATIVE CALCULATIONS

Table 1 shows the common soil chemical and management properties used in the simulations for lindane and 2,4-D (acid). In later papers, we will examine the influence of variations in several of these parameters, but for the present analysis they will be kept constant at the values given. Table 2 summarizes the benchmark properties of lindane and 2,4-D (acid) obtained from the literature at the standard temperature of 25°C. These values are subject to uncertainties, which will be shown to have an influence on results in a later paper.

The combination of the common and benchmark properties in Tables 1 and 2, the diffusion coefficient definitions (Eq. [7] and [8]), and the effective diffusion coefficient definition (Eq. [13], [14], and [18]) yield the lindane and 2,4-D effective diffusion coefficients, D_E , plotted in Fig. 1 as a function of water content. For lindane, the respective contributions add to a relatively constant diffusion coefficient over much of the range of water content, which implies that the water content effects on diffusive processes should not be significant. This conclusion is consistent with the lindane experimental data for D_E presented by Shearer et al. (1973), which showed very little variation with water content. Their somewhat higher D_E values compared with Fig. 1 could be explained by the low organic matter of the Gila silt loam soil they studied.

The 2,4-D diffusion coefficient, on the other hand, is dominated by liquid diffusion and changes by over three orders of magnitude as a function of water content. The calculated values at saturation are similar to the D_E measurements for 2,4-D of Lindstrom et al. (1968) taken on nine saturated soils.

Figure 2 shows pesticide concentrations remaining at 30 d as a function of depth when the pesticides were subject to 5 mm/d water evaporation, no water evaporation, or 30 d of leaching at 5 mm/d. It is clear from this figure that the high adsorption affinity for lindane keeps it localized near the region where it was incorporated initially, whereas 2,4-D is quite mobile. Furthermore, the lindane curve is only slightly affected by dif-

Table 2—Physical-chemical properties of lindane and 2,4-D at 25°C.

Property	Lindane			2,4-D		
	Value	Reference	Comments	Value	Reference	Comments
Saturated vapor density, C_G^* (g/m ³)	10 ⁻³	Spencer & Cliath, Cliath, 1970	Measured by gas saturation 20–60°C	5 × 10 ⁻⁶	Goring, 1967	Method not specified
Solubility, C_L^* (g/m ³)	7.5	Freed, 1976		900	Herbicide Handbook, 1974	Herbicide Handbook, acid
Organic carbon partition coefficient, K_{oc} (m ³ /kg)	1.3 ± 16%	Rao & Davidson, 1980	Mean of seven soils	2 × 10 ⁻² ± 7%	Rao & Davidson, 1980	Mean of nine soils
Degradation coefficient, μ (per day)	2.67 × 10 ⁻³	Rao & Davidson, 1980	Aerobic lab studies	4.62 × 10 ⁻³	Rao & Davidson, 1980	Laboratory data
Henry's constant, K_H	1.33 × 10 ⁻⁴		$K_H = C_G^* / C_L^*$	5.5 × 10 ⁻⁹		
Half-life, $T_{1/2}$ (days)	260		$T_{1/2} = 1n2/\mu$	15		

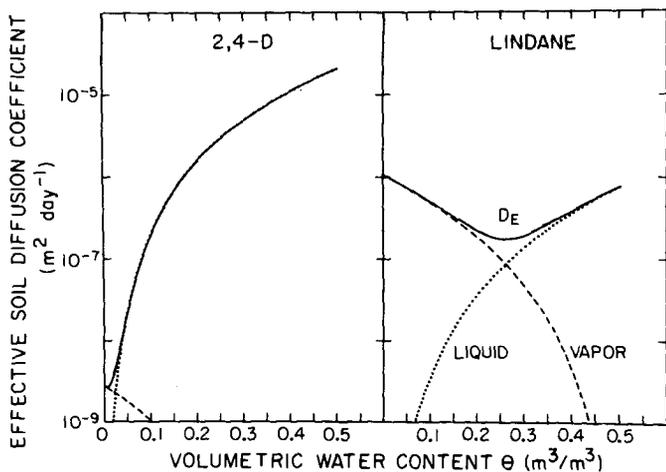


Fig. 1—Effective soil diffusion coefficient calculated for lindane and 2,4-D as a function of water content.

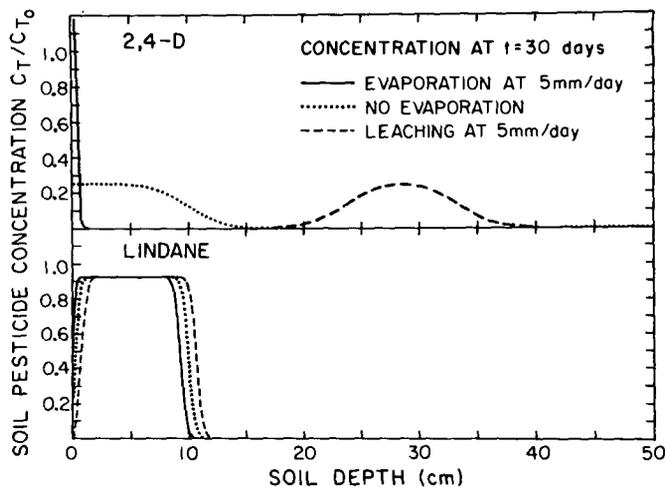


Fig. 2—Calculated lindane and 2,4-D concentrations remaining at 30 d.

fusion and degradation, whereas 2,4-D is significantly depleted by degradation and spread out by diffusion. Figure 3 shows volatilization flux rates given (kg/ha per day) for three cases (volatilization occurring with evaporation rates of 0, 2.5, and 5 mm/d for a soil with $f_{oc} = 0.0125$). For both chemicals, volatilization can be significantly enhanced by upward water flow, which substantiates the experimental observations of Spencer and Cliath (1973) for lindane in volatilization chambers. This chemical is predicted to have a much more significant volatilization enhancement due to water flow than did triallate in the experiments of Jury et al. (1980). Although the volatilization of 2,4-D is increased significantly with evaporation, it remains quite small compared with lindane.

Table 3 shows the influence of organic C and depth of incorporation on cumulative lindane and 2,4-D volatilization over a 30-d period without water evaporation. Volatilization at two boundary layer thicknesses are given: 5.0 mm and 0.5 mm. The thinner boundary layer corresponds to a well-mixed surface condition (e.g., due to high wind velocity, which causes the pesticides to deplete more rapidly from the surface). As shown in this table, volatilization of lindane, particularly for shallow incorporation, represents a significant loss pathway, whereas for 2,4-D, the loss is negligible. Reduction of boundary layer thickness by a factor of 10 increases lindane volatilization (but not proportionally) indicating that the concentration of lindane at the surface is low (i.e., well-mixed), even at the larger boundary layer thickness.

The influence of water evaporation on volatilization is shown in Table 4 for both chemicals. The values of 2,4-D are higher than in the absence of evaporation, but are still relatively unimportant. Lindane on the other hand could lose up to 68% of the initial amount in 30 d of evaporation-aided volatilization.

Persistence of the chemicals at 30 d is summarized in Table 5 as a percent of initial application. The insensitivity of persistence of 2,4-D to placement, water flow, and soil conditions indicates that degradation is the dominant loss pathway. Persistence of lindane varies significantly with all of these factors, so that volatilization losses could contribute significantly to

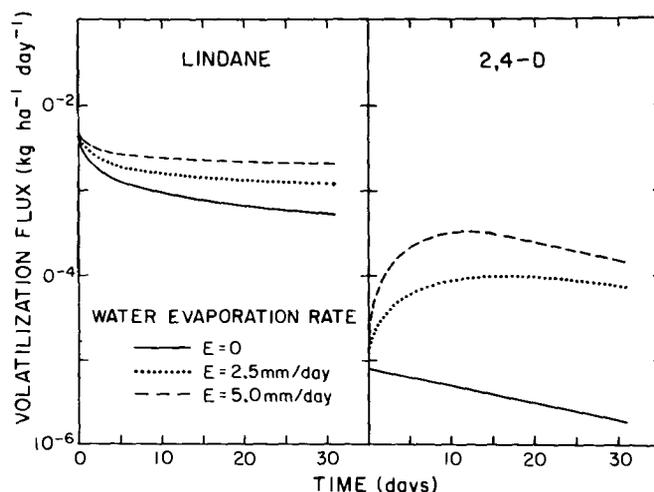


Fig. 3—Calculated lindane and 2,4-D surface volatilization fluxes when water evaporation is occurring.

Table 3—Cumulative volatilization after 30 d, expressed as a percent of the 1 kg/ha amount initially incorporated, when no water evaporation is occurring.

Lindane				2,4-D			
$f_{oc} = 0.0125$		$f_{oc} = 0.0250$		$f_{oc} = 0.0125$		$f_{oc} = 0.0250$	
$d = 5.0$ mm	$d = 0.5$ mm	$d = 5.0$ mm	$d = 0.5$ mm	$d = 5.0$ mm	$d = 0.5$ mm	$d = 5.0$ mm	$d = 0.5$ mm
$L = 1$ cm							
28.4	32.6	19.1	23.2	0.1	0.7	0.1	0.5
$L = 10$ cm							
2.9	3.3	1.9	2.3	≈ 0	0.1	≈ 0	0.1

errors in the measurement and interpretation of apparent degradation rate calculated from persistence data and Eq. [6].

SUMMARY AND CONCLUSIONS

The calculations above with lindane and 2,4-D illustrate the variety of outputs available with the screening model. The significant differences in behavior between

Table 4—Cumulative volatilization after 30 d, expressed as a percent of the 1 kg/ha amount initially incorporated, when water evaporation is occurring.

Lindane				2,4-D			
$f_{oc} = 0.0125$		$f_{oc} = 0.0250$		$f_{oc} = 0.0125$		$f_{oc} = 0.0250$	
$E =$ 2.5 mm/d	$E =$ 5.0 mm/d						
$L = 1 \text{ cm}$							
45.9	67.6	27.9	41.3	0.5	0.9	0.3	0.6
$L = 10 \text{ cm}$							
4.7	7.4	2.8	4.2	0.2	0.7	0.1	0.4

Table 5—Persistence of chemicals, expressed as a percent of the 1 kg/ha amount initially incorporated remaining at 30 d, as a function of E , L , and f_{oc} .

Lindane						2,4-D					
$f_{oc} = 0.0125$			$f_{oc} = 0.0250$			$f_{oc} = 0.0125$			$f_{oc} = 0.0250$		
$E =$ 0	$E =$ 2.5	$E =$ 5.0	$E =$ 0	$E =$ 2.5	$E =$ 5.0	$E =$ 0	$E =$ 2.5	$E =$ 5.0	$E =$ 0	$E =$ 2.5	$E =$ 5.0
mm/day											
$L = 1 \text{ cm}$											
66	49	28	74	66	53	25	25	25	25	25	25
$L = 10 \text{ cm}$											
90	88	85	91	90	89	25	25	25	25	25	25

the two chemicals in identical circumstances show how the model might be used to identify the major loss pathways for a given chemical and to determine the relative mobility, volatility, or persistence of a group of chemicals. In later papers we will illustrate these potential applications in greater detail.

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