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Use of Models for Assessing Relative Volatility, Mobility, and Persistence of Pesticides and Other Trace Organics in Soil Systems

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I. INTRODUCTION

In our modern society pesticides are a necessity. Even under optimal conditions our capacity for food production is inadequate to prevent starvation for millions of people. For many crops, application of pesticides means the difference between success and failure for the local farmer, and thus has become as necessary a procedure for farming as is fertilizer. Unfortunately, the toxicity of a given pesticide is not specific to the insect or weed it was designed to control. For this reason there is a potential health hazard associated with migration of the organic chemical to places of exposure for humans or animals. These migratory pathways may be quite complex, occurring aerially at the time of application, through volatilization at the soil surface, through leaching to underground waterways, or through runoff to surface waters.

The complex requirements of pesticides—effective and specific toxicity and low environmental risk—have spawned a massive search on the part of pesticide manufacturing companies for new and effective chemicals. Although there exist straightforward procedures for screening these candidate chemicals for dose effectiveness, considerably less is known about methods for assessing environmental risk. Consequently, decisions to release chemicals for use have sometimes been based on poorly defined criteria for identifying the potential environmental harm of a chemical prior to its use in a commercial operation.

Assessment of the pollution potential of these chemicals is an extremely difficult problem. In order to control pests effectively within the crop root zone, the ideal pesticide must have mobility, persistence, and reactive properties within a relatively narrow range. Given the large number of chemicals proposed each year and the long travel times to various exposure sites, it seems inevitable that simulation models will play a significant role in evaluating candidate chemicals. Although ideally these simulation models would be capable of making quantitative projections of pollutant migration in a given setting, the significant variability of soil-water and chemical-transport properties under field settings makes such an outcome difficult to achieve (*3*, *50*). Instead, it seems most likely that a pesticide simulation model will be useful first as a means of screening various pesticides for their behavior under prototype conditions. Second, such a model could be used to identify the significant physical–chemical properties of a proposed pesticide which must be known in order to make a reasonable assessment of its pollution potential. In addition to identifying these critical properties, the model could estimate the sensitivity of its own simulations to uncertainties in the values of these properties. Finally, the model could be useful in identifying areas in need of future research.

The purpose of this article is to present such a model and to demonstrate its usefulness. We first review the significant pathways of loss for a soil-applied pesticide. Second, we introduce a prototype simulation model to be used for screening the behavior of pesticides with respect to volatility, mobility, and persistence. Finally, we apply this screening model to a collection of 20 pesticides for which we have gathered experimental information from the literature, and demonstrate in a series of simulations how this model may be used to assess the pesticides' relative behavior in given circumstances. Although we will restrict our analysis to pesticides, the screening approach used is equally applicable to other trace organics for which benchmark chemical information is available.

II. PATHWAYS OF PESTICIDE LOSS IN SOIL

Once a pesticide reaches the soil, it follows one of several possible pathways, including volatilization, leaching, degradation and/or transformation reactions, precipitation, runoff into surface waters, or retention in the soil as bound residues. Several of these are discussed below. We do not discuss the pathway of loss in surface runoff, which is highly site-specific and is treated in considerable detail in the CREAMS watershed model (*39*).

A. Volatilization

Volatilization refers to gaseous loss of pesticide to the atmosphere through the soil surface. Air transport of pesticides is probably the principal method of their widespread dispersion in the environment. Since the soil obviously becomes a residence for a large portion of the pesticides that are applied to crops, the ability to predict and control volatilization of pesticides from soil is important in decreasing environmental contamination with pesticides. Recent reviews on volatilization include those by Hamaker (*27*), Spencer *et al.* (*64*, *68*), Wheatley (*73*), Guenzi and Beard (*24*), Plimmer (*53*), and Taylor (*71*).

Potential volatility of a chemical is related to its inherent vapor pressure, but actual vaporization rates depend on the environmental conditions and on all other factors that control behavior of the chemical at the solid–air–water interface. Volatilization of pesticides from nonadsorbing surfaces is directly proportional to their relative vapor pressures, but volatilization from soil depends upon many parameters affecting their adsorption, movement, and persistence. Volatilization from soil involves desorption of the pesticides from the soil, movement to the soil surface, and vaporization into the atmosphere (*64*).

The rate at which a pesticide moves away from the surface is controlled by diffusion. Close to the evaporating surface there is relatively little movement of air and the vaporized substance is transported from the surface through the stagnant air layer only by molecular diffusion. The actual rate of mass transfer away from the surface by diffusion will be proportional to the diffusion coefficient and to the vapor density of the pesticide at the evaporating surface. Since the thickness of the stagnant air layer depends on air flow rate and turbulence, surface geometry and surface roughness can alter air flow effects through their influence on air turbulence. Thus, gaseous loss is influenced strongly by the type of soil cover and the atmospheric conditions, i.e., wind in the vicinity of the soil surface. In general, under a given set of conditions, as air exchange rate or air turbulence increases volatilization rate increases.

Every chemical has a characteristic saturation vapor pressure or vapor density, which varies with temperature. Vapor pressure is the key chemical characteristic controlling pesticide vapor behavior. Knowledge of vapor pressure, along with other basic physical–chemical properties of water solubility, adsorption, and persistence, can be used to estimate relative volatilization rates of pesticides from soil. Since the vapor pressure of many pesticides increases three- to four-fold for each 10°C increase in temperature, reliable values for vapor pressure at various temperatures are necessary to estimate vapor losses or to predict their partitioning among soil, water, and air. The gas saturation method of measuring vapor pressure has proven to be reliable for measuring vapor pressures of a wide variety of pesticides with vapor pressures as low as 10^{-2} mPa (*67*).

Vapor pressures of pesticides are greatly decreased by their interaction with soil, mainly due to adsorption. Spencer *et al.* (*60*) reported that the magnitude of the reduction in vapor pressure in the soil due to adsorption is dependent mainly on the nature of the pesticide, its concentration, the soil water content, and soil properties, particularly soil organic matter content. The concentration of the desorbed pesticide in the soil water dictates the vapor density of the pesticide in the soil air in accordance with Henry's law. This means that the amount of a pesticide that must be adsorbed to create a saturated solution is the same as that required for a saturated vapor and for any fraction of solution or vapor saturation. Hence, soil-water adsorption coefficients can be used to calculate relative vapor densities in the soil atmosphere. A desorption isotherm at one temperature is adequate for predicting vapor density and solution concentrations at other temperatures from the known relationship between vapor pressure, solubility, and temperature.

For weakly polar or non-ionic pesticides, the amount of soil organic matter is the most important soil factor for increasing adsorption and, consequently, for decreasing vapor pressure or potential volatility of the chemical in soil. Since most of the more volatile pesticides are only weakly polar or non-ionic, their adsorption and, therefore, volatility depend on soil organic matter content (*64*).

For adsorption of weakly polar pesticides by soil, water content effects are also especially important, and relatively low soil concentrations are needed for a saturated vapor. The vapor pressure of weakly polar compounds in soil increases greatly with increases in concentration and temperature, but decreases markedly when the soil–water content decreases to less than one molecular layer of water (*60*). Water contents greater than one molecular layer have little or no effect on pesticide vapor densities in soil, but higher water contents do greatly affect volatility through their effects on pesticide movement through the soil.

When a pesticide is mixed into the soil, the initial volatilization rate will be a function of the vapor pressure of the chemical at the surface as modified by adsorptive interactions with the soil. As the concentration at the surface of the soil changes, volatilization becomes dependent on the rate of movement of the pesticide to the soil surface (*14, 15, 63*). Two general mechanisms whereby pesticides move to the evaporating surface are diffusion and convection, or mass flow, in evaporating water. The two mechanisms usually operate together in the field, where water and the pesticides vaporize at the same time. When water is not evaporating, the volatilization rate depends on the rate of movement of the pesticide to the soil surface by diffusion. Pesticides can diffuse through soil in both vapor and nonvapor phases, and in general pesticide diffusion rates are controlled by the same factors that control their vapor pressure; i.e., temperature and variables affecting adsorption, such as chemical concentration and the water, organic matter, and clay content of the soil (*11*). In addition, soil bulk density, or degree of soil compaction, influences the rate of diffusion, particularly gaseous diffusion (*15*). Diffusion processes in the soil may control volatilization losses of pesticides even in the presence of evaporating water if the pesticide does not move significantly by mass transfer with the water due to its insolubility or its much greater mobility in the vapor than in the liquid phase of the soil system (*16*).

Volatilization may be enhanced by upward water flow, which tends to bring dissolved chemicals to the site of volatilization. When water evaporates from the soil surface, the suction gradient toward the surface causes appreciable upward movement of water, and any pesticides in the solution will move toward the surface by mass flow (convection) with the evaporating water. Spencer and Cliath (*63*) demonstrated experimentally that this phenomenon, called the wick effect, accelerates volatilization of pesticides. The magnitude of the wick effect depends on the adsorption characteristics and water solubility of the pesticide and other factors affecting partitioning between the air, water, and solid phases in the soil.

Vaporization of pesticides from soil can be estimated from consideration of the physical and chemical factors controlling concentrations at the soil surface. Most models developed for estimating volatilization rates of soil-incorporated pesticides are based on equations describing the rate of movement of the pesticide to the surface by diffusion and/or convection (*34*). In addition to factors directly affecting movement and vapor behavior, the proportion of a pesticide in soil that will be lost by volatilization or leaching depends on the resistance of the chemical to degradation.

B. Leaching

Leaching refers to the downward movement of an organic chemical as a dissolved constituent in the solution phase. It is therefore a function not only of the downward water flux but also of the concentration of chemical in the liquid phase. Numerous laboratory studies have shown that prediction of the extent of leaching for pesticides depends most critically on knowledge of the partitioning of the pesticides between the solid and solution phases of the soil. Discussions of these studies are available elsewhere (*2*, *41*, *43*). Thus, the same partitioning between the solid and solution phases which determines the vapor density of a pesticide in the soil air as discussed in the previous section also determines the concentration in the solution phase available for leaching. The soil–water adsorption isotherm provides a direct measure of the partitioning and of the effect of the factors—nature of the pesticide, its concentration, temperature, soil-water content, soil properties—that influence the distribution.

The use of the adsorption isotherm for determining pesticide distribution, its methods of measurement, and the many soil, pesticide, and environmental factors that can influence its value have been the subjects of considerable research in the last 2 decades. These topics have been dealt with extensively in several excellent reviews (*1, 8, 22, 28, 31, 32, 55*).

For purposes of predicting the leachability of a pesticide, the linear adsorption isotherm presents the simplest approach. When the isotherm is linear, the slope of the isotherm, called the distribution coefficient, K_D, is sufficient to partition a given concentration into the solid and solution phases. When the isotherm is nonlinear, or nonreversible, or when the exchange between the liquid and solid phases is rate-limited, the description becomes more complex and requires more extensive data acquisition as well as computer methods to predict behavior. Karickhoff *et al.* (*35, 36*) have shown that for low aqueous concentrations of weakly polar compounds the linear isotherm is an accurate representation of the adsorption isotherm. Rao and Davidson (*55*) have reviewed the current theory for dealing with isotherms that are nonlinear, nonreversible, or that depend on rate-limited processes.

Soil organic matter has been shown to be the single most important soil property affecting pesticide adsorption. The large variability in the distribution coefficient K_D of a pesticide due to adsorption by different soils can be greatly reduced by normalizing adsorption based on the organic carbon content of the soil (K_{oc}). Lambert *et al.* (*40*) were able to show a nearly constant partition coefficient for pesticide adsorption by several soils. Hamaker and Thompson (*28*) and Rao and Davidson (*55*) have tabulated K_{oc} values from the literature for a number of pesticides on a variety of soils, many covering a wide range of organic carbon contents.

Measured distribution coefficients are not always available for a particular compound. Significant progress has been made in our ability to estimate adsorption parameters, and many of these estimates have been highly useful, depending on the level of accuracy required (*6, 9, 35, 36, 38, 45, 55*).

The octanol–water partition coefficient has had wide application in predicting the partitioning of weakly polar organic compounds in biological systems. Briggs (*6*) used the octanol–water partition coefficient K_{ow} to predict a distribution coefficient for soils, which showed a high correlation with the measured adsorption of several pesticides by soils. Rao and Davidson (*55*) have recently summarized the use of the K_{ow} for predicting pesticide adsorption in soils.

Distribution coefficients, either measured via an isotherm or estimated, are useful indices of pesticide leachability because of their relative ease of determination. Another index of the leachability of a pesticide is the soil thin-layer chromatography (TLC) method (*30*). This method is particularly useful because it is relatively rapid and allows the comparison of a large number of soil types. In addition, the results of soil TLC, the R_F values, correlate well with K_{oc} and K_{ow} values (*30, 31*).

C. Degradation

Degradation refers to the combined biological, chemical, or photochemical transformation of the pesticide subsequent to application. Although these individual processes may be analyzed quantitatively, for the most part degradation has been empirically represented in terms of a half-life or reaction coefficient that lumps all transformations together into an effective first-order process. Only limited information is available about the individual reaction rates and this information has been widely scattered because of the difficulty in making measurements under natural conditions. Degradation has often been represented merely as the difference between final and initial quantities of chemical that are solvent-extractable from the soil. In this method of analysis, volatilization and also any bound nonextractable residues will be included as part of the degradation term.

Of the three degradation processes listed above, photooxidation is normally important only during application and plays a minimal role once the pesticide has been incorporated into the soil. Microbial degradation may occur under both aerobic and anaerobic conditions, with the latter frequently enhancing decomposition (*55*). Chemical reactions are widespread in soil, and may be either oxidation transformations, hydrolytic nucleophilic transformations, or nonhydrolytic nucleophilic displacement reactions (*21*). Comprehensive summaries of measured rate constants for many pesticides are given in Rao and Davidson (*55*) and Nash (*47*).

D. Precipitation

Chemical precipitation refers to the formation of a crystalline and solid phase when the concentration of organic chemical in solution exceeds the solubility. This process, not generally recognized to occur with pesticides in soil, would most likely occur with sparingly soluble pesticides of low vapor pressure when upward water flow causes an accumulation at the surface. Only to the degree to which redissolution is more strongly rate-limited than precipitation would this process be considered an actual loss pathway from soil.

E. Bound Residues

As mentioned in most studies dealing with pesticide persistence in soils the pesticide residual level in the soil is measured by extraction with organic solvents. However, other studies dealing with ^{14}C-labeled pesticides have shown that in some cases a substantial fraction of applied pesticide is apparently bound to the soil and cannot be recovered by exhaustive extraction with organic solvents (*37*). A recently formulated working definition of a soil-bound pesticide residue is "that unextractable and chemically unidentifiable pesticide residue remaining in fulvic acid, humic acid, and humin fractions of the soil after exhaustive sequential extraction with nonpolar organic, and polar solvents" (*37*). The existence of soil-bound residues means that pesticides previously classified as nonpersistent in soils may actually be considerably more persistent when the bound residues are taken into account. The exact mechanisms of pesticide binding to soil are generally unknown, however, so that there is no method at present for estimating the extent of binding in any given circumstance. Further, since virtually all measurements of soil half-lives consider bound residues as part of the degradative loss, they will probably continue to be counted as such, both in modeling and assessment.

III. BENCHMARK PROPERTIES NEEDED TO PREDICT PESTICIDE LOSS FROM SOILS

In the previous section a qualitative description was given of the major pathways of pesticide loss in soil. In this section we attempt to define a minimum set of chemical and physical characteristics for each organic chemical that must be known in order to make a reliable assessment of the extent of loss through these pathways. The emphasis will be on determining relative behavior of different pesticides under prototype conditions.

A. Phase Partitioning Coefficients

Since a pesticide moves in both the liquid and vapor phase but is stored in many cases primarily in the adsorbed phase, it is essential to know how a given quantity of applied chemical will partition among these three phases in the soil.

The adsorbed-liquid partitioning is expressed through an adsorption isotherm. At low concentrations the shape of this isotherm may in many cases be approximated by a straight line (*35*, *36*) giving rise to the following simple linear relationship:

$$C_S = K_D C_L \tag{1}$$

where C_S is adsorbed concentration (μg/g), C_L is solution concentration (μg/cm^3 soil solution), and K_D is the slope of the adsorption isotherm or the distribution coefficient. Since this distribution coefficient, for nonionic pesticides at least, primarily represents adsorption to organic matter, variability between soils may be eliminated to an extent by defining an organic carbon distribution coefficient

$$K_{oc} = K_D/f_{oc} \tag{2}$$

where f_{oc} is the fraction of organic carbon in the soil. This standardization greatly decreases the coefficient of variability for a given pesticide in different soils (*28*).

When measured adsorption values are not available, good correlation has been found between K_{oc} and the octanol–water partition coefficient K_{ow}. Rao and Davidson (*55*) recommended the regression

$K_{oc} = 1.6\, K_{ow}$

$$\log K_{ow} = 1.029 \log K_{oc} - 0.21; \qquad r^2 = 0.91 \tag{3}$$

The liquid–vapor partition, as mentioned above, is generally represented by Henry's law:

$$C_G = K_H C_L \tag{4}$$

where C_G is the gas concentration of pesticide (μg/cm^3 soil air) and K_H is the Henry's law constant. Since studies have shown that this relationship persists to saturation in many circumstances, the Henry's law constant may be calculated as the ratio of saturated vapor density to pesticide solubility:

$$K_H = C_G^*/C_L^* \tag{5}$$

where * refers to saturation values.

B. Degradation Coefficients

Since 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 first-order degradation rate is assumed and the rate constant μ (day^{-1}) is measured by the rate equation

$$M(t) = M(0)\exp(-\mu t) \tag{6}$$

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, since measurements of μ vary enormously from field to lab, and since in the past the degradative losses have often been mixed in with other unmeasured pathways of loss, this parameter is both extremely important and extremely difficult to assess. For example, Hamaker (*27*) reports a half-life for simazine of 105 days (±34%), which contrasts with values of 75 days (lab) and 64 days (field) given by Rao and Davidson (*55*) and with 55 days (±63%) given by Nash (*47*).

C. Diffusion Coefficients

Other than mass flow within moving soil solution, the two dominant flow pathways 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 (*49*). This tortuosity factor is a function of volumetric air content a and of soil geometry, and has been described using a variety of models (*56*). One such model, which has proved useful for describing pesticide soil diffusion coefficients, is the Millington–Quirk model (*14, 57*). With this model, we obtain for the soil gas diffusion coefficient

$$D_G = (a^{10/3}/\phi^2)D_G^{air} \tag{7}$$

where ϕ is the soil porosity.

Since the Millington–Quirk tortuosity formula has no 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 (*5*) and by using the Fuller correlation (*52*), 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 $D_G^{air} = 0.05$ cm^2/sec is adequate for most pesticides, and D_G^{air} need not be measured in every case.

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

$$D_L = (\theta^{10/3}/\phi^2)D_L^{water} \tag{8}$$

where $\theta = \phi - a$ is the volumetric water content. Although few if any water liquid diffusion coefficient measurements have been made on pesticides, this coefficient seems to differ only slightly among other organic compounds of similar molecular weight (*7*). From this compilation, we chose $D_L^{water} = 5 \times 10^{-6}$ cm^2/sec as a representative value for all pesticides.

In summary, among the primary properties we have discussed it is essential to measure the organic carbon partition coefficient, the saturated vapor density, the solubility, and the degradation half-life for each chemical. As we also mentioned, 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.

IV. THEORY

The screening model to be introduced is essentially that described in Jury *et al.* (*34a*) and 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 a pesticide will move under a given set of imposed circumstances, by describing the behavior of one chemical relative to another. 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.

- 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 constant organic carbon fraction f_{oc}
- Linear, equilibrium adsorption isotherm so that Eq. (1) is valid
- Linear, equilibrium liquid–vapor partition [Henry's law, Eq. (4)]
- Uniform initial incorporation of pesticide at time $t = 0$ between the surface and depth L
- 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 and simplified using these assumptions.

A. 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

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_S}{\partial z} + \mu C_T = 0 \tag{9}$$

where C_T = mass of solute per soil volume (μg/cm^3), J_S = solute mass flow per soil area per time (μg/cm^2/day), and μ = degradation rate (day^{-1}).

B. Flux Equation

The mass flux may be written (ignoring adsorbed material transport) as

$$J_S = -D_G \frac{\partial C_G}{\partial z} - D_L \frac{\partial C_L}{\partial z} + J_W C_L \tag{10}$$

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, by Eqs. (7) and (8).

C. Concentration

Total solute concentration is made up of contributions from each phase:

$$C_T = \rho_b C_S + \theta C_L + a C_G \tag{11}$$

Equations (9), (10), and (11) may be combined to form a second-order transport 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. The linear equilibrium approximations in Eqs. (1) and (4), however, allow us to rewrite Eqs. (9) and (10) in terms of only one of the variables. Thus, Eq. (11) may be written as

$$C_T = R_S C_S = R_L C_L = R_G C_G \tag{12}$$

where

$$R_S = \rho_b + \theta/K_D + aK_H/K_D \tag{13}$$

$$R_L = \rho_b K_D + \theta + aK_H \tag{14}$$

and

$$R_G = \rho_b K_D/K_H + \theta/K_H + a \tag{15}$$

are the partition coefficients for the solid, liquid, and gaseous phases, respectively. The expressions in Eqs. (13)–(15) give the ratio of the total concentration C_T to the concentration in each respective phase.

Equations (12)–(15) allow us to rewrite Eqs. (9) and (10) solely in terms of the total concentration, leaving us with

$$J_S = -D_E \frac{\partial C_T}{\partial z} + V_E C_T \tag{16}$$

$$\frac{\partial C_T}{\partial t} = D_E \frac{\partial^2 C_T}{\partial z^2} - V_E \frac{\partial C_T}{\partial z} - \mu C_T \tag{17}$$

where D_E is the effective diffusion coefficient, given by

$$D_E = \frac{D_G}{R_G} + \frac{D_L}{R_L} \tag{18}$$

and V_E is the effective solute convection velocity, given by

$$V_E = J_W/R_L \tag{19}$$

We could just as easily have written Eqs. (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.

D. Prototype Screening Simulations

In a typical field situation a pesticide is applied to a soil layer (surface or incorporated) and is 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 and managerial index for classifying pesticides into categories. As mentioned above, we propose the following scenario as such a screening tool:

- Uniform incorporation of a quantity M (kg/ha) of chemical to a depth L (cm) below the surface
- Volatilization through a stagnant surface layer of thickness d
- Convection by a steady water flux $J_W = \pm J$ or 0
- 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 are as follows.

E. Boundary Conditions

1. Initial condition:

$$\begin{array}{ll} C_T(z,0) = C_0 & \text{if} \quad 0 < z < L \\ C_T(z,0) = 0 & \text{if} \quad z > L \end{array} \tag{20}$$

where C_0 is the uniform initial concentration. If C_0 is given in μg/cm^3 of soil, M in kg/ha, and L in cm, then $C_0 = 10M/L$.

2. Upper boundary condition:

$$J_S(0,t) = -hC_G(0,t) \tag{21}$$

where $h = D_G^{\text{air}}/d$ 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):

$$-D_E\, \partial C_T/\partial z + V_E C_T = -H_E C_T \qquad \text{at} \quad z = 0 \tag{22}$$

where $H_E = h/R_G$.

3. Lower boundary condition:

$$C_T(\infty, t) = 0 \tag{23}$$

F. Solutions to Equations

If we neglect the possibility of chemical precipitation, we may solve Eqs. (17), (20), (22), and (23) analytically to give

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

Using Eqs. (16), (22), and (24) we may write the volatilization flux at the surface as

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

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.

G. Boundary Layer Model

By assumption, both evaporation rate E and pesticide volatilization flux J_S are limited by diffusion through the stagnant air layer of thickness d above the soil surface. Therefore, since we specify evaporation rate, the diffusion layer thickness is also specified. To see this, one writes the water and pesticide diffusion equations across the air layer:

1. Water vapor transport

$$E = \frac{D_{WV}^{air}}{d\rho_{WL}} [\rho_{WV}(0) - \rho_{WV}(d)] \tag{26}$$

2. Pesticide vapor transport

$$J_S = \frac{D_G^{air}}{d} [C_G(0) - C_G(d)] \tag{27}$$

where ρ_{WV} is water vapor density and ρ_{WL} is liquid water density. If we further assume that ρ_{WV} is saturated at the surface, that the relative humidity R.H. is 0.5 at d, that $C_G(d) = 0$, and that no evaporation occurs at night, we arrive at the final relation for d:

$$d = D_{WV}^{air} \rho_{WV}^{*}(1 - \text{R.H.})/2E\rho_{WL} \tag{28}$$

Equation (28) was used in all the following calculations in which upward water flux was nonzero. In calculations for which $E = 0$, d was given a specified value of 4.75 mm, the value that corresponds to $E = 2.5$ mm/day in Eq. (28).

The layer of stagnant air may or may not form a significant barrier to volatilization loss for a given pesticide, depending on a variety of factors. In general, if the diffusion rate through the air layer [Eq. (27)] is able to match the upward flux to the soil surface without having the surface concentration build up, then the stagnant layer is not acting as a barrier to loss and the volatilization flux will not depend strongly on the thickness of the boundary layer. Conversely, if the diffusion rate through the air layer is less than the flow to the surface by diffusion or mass flow, then the concentration at the soil surface will not be close to zero and the thickness of the air layer will regulate the loss by volatilization. We will call chemicals which behave in this manner "boundary-layer controlled" (*34b*).

H. Cumulative Losses

The model calculations are oriented toward screening tests. To that end we summarize cumulative volatilization, degradation, and persistence as a percent of the initial mass as follows.

1. Cumulative volatilization:

$$\%V = 100\left[\int_0^t J_S(0, t')\,dt'\right]\Big/M(0) \qquad (29)$$

where J_S is given by Eq. (25).

2. Cumulative degradation:

Cumulative degradation percentage is given by

$$\%D = 100 - \%V - \%M(t) \qquad (30)$$

where $M(0) = C_0L$ is the initial mass present and

$$\%M(t) = 100\left[\int_0^\infty C_T(z', t)\,dz'\right]\Big/M(0) \qquad (31)$$

is the remaining mass at time t. The integrals in Eqs. (29) and (31) are evaluated numerically using the analytic solution.

V. CHEMICALS AND PROPERTIES USED IN SCREENING TESTS

A. Benchmark Properties

Tables I through IV summarize the physical and chemical properties of the 20 pesticides we have chosen to illustrate the screening model. Table I gives vapor densities and vapor pressures for the chemicals, ranging from a high of 2800 mPa (2.1×10^{-2} mm Hg) for EPTC to a low of 0.002 mPa (1.5×10^{-8} mm Hg) for simazine. Table II gives water solubilities for the chemicals, ranging from a high of 900 mg/liter for

TABLE I

Vapor Pressure and Vapor Density for Pesticides Used in Screening Tests

Chemical	Vapor pressure (mPa)[a]	Vapor density (μg/liter)	Reference	Comments
Atrazine	0.090	0.008	*18*	Gas saturation method, 50–130°C
Bromacil	0.029	0.003	*12*	Estimated from 107 mPa value at 100°C with H_v of lindane[b]
Carbofuran	1.120	0.100	*10*	Knudsen effusion method, 33 and 50°C
2,4-D	0.051	0.005	*20*	No method given
DDT	0.045	0.006	*62*	Gas saturation method, 20–40°C
Diazinon	16.132	1.980	*29*	Gas saturation method, 20–100°C
Dieldrin	0.677	0.100	*59*	Gas saturation method, 20–40°C
Diuron	0.016	0.002	*48*	Estimated from one value: 0.036 mPa at 30°C
EPTC	2800	220	*51*	Estimated from values at 23, 24, and 28°C
Ethoprophos	46.66	4.50	*46*	From manufacturer's technical bulletin
Lindane	8.63	1.00	*61*	Gas saturation method, 20–40°C
Methyl parathion	2.400	0.250	*66*	Gas saturation method, 24–45°C
Monuron	0.023	0.002	*74*	Thermogravimetry method, 30–105°C, calculated at 25°C
Napropamide	0.533	0.058	*33*	Method not reported
Parathion	1.256	0.147	*66*	Gas saturation method, 25–45°C
Phorate	148	15.5	*69*	Gas saturation method, 35–75°C
Prometryne	0.284	0.027	*18*	Gas saturation method, 50–103°C extrapolated to 25°C
Simazine	0.002	1.7×10^{-4}	*18*	Gas saturation method, 50–103°C extrapolated to 25°C
Triallate	25.73	3.17	*23*	Gas saturation method, 20–45°C
Trifluralin	14.80	2.00	*65*	Gas saturation method, 20–40°C

[a] 1 mPa = 7.5×10^{-6} mm Hg.

[b] H_v = heat of vaporization.

TABLE II

Water Solubility of Pesticides Used in Screening Tests

Chemical	Solubility (mg/liter)	Reference	Comments
Atrazine	32	*17*	Mean of three studies
Bromacil	815	*33*	Herbicide handbook
Carbofuran	320	*4*	19°C
2,4–D	900	*33*	Herbicide handbook; acid
DDT	0.003	*25*	
Diazinon	40	*38*	
Dieldrin	0.15	*13*	
Diuron	37	*17*	Recording spectrophotometer
EPTC	370	*33*	Herbicide handbook
Ethoprophos	750	*42*	
Lindane	7.5	*17*	
Methyl parathion	57	*38*	
Monuron	262	*33*	
Napropamide	73	*33*	
Parathion	24	*38*	
Phorate	50	*38*	
Prometryne	48	*38*	
Simazine	5	*17*	
Triallate	4	*34*	
Trifluralin	0.3	*70*	

2,4-D (acid) to a low of 0.003 mg/liter for DDT. Table III summarizes the organic carbon partition coefficients obtained for the 20 chemicals, together with the coefficient of variation and number of soils used to obtain the average. The amount of available information varies widely, ranging from measurements on over 100 soils for simazine to several chemicals for which K_{oc} had to be calculated from an octanol–water partition coefficient K_{ow} measurement according to the regression equation (3) taken from Rao and Davidson (*55*). K_{oc} values range from 243,120 (DDT) to 20 (2,4-D). Table IV summarizes available information on degradation half-lives, together with references and comments where appropriate. Half-life values for a given chemical varied enormously in different studies, depending on whether the measurements were taken in the laboratory or in the field and depending on whether the conditions were aerobic or anaerobic.

B. Common Properties

Table V gives the standardized values of soil, atmosphere, water, and management properties that will be used in the simulations. Coefficients

[a] 1 mPa = 7.5 × 10^{-6} mm Hg.

[b] H_v = heat of vaporization.

TABLE III

Organic Carbon Partition Coefficients K_{oc} for Pesticides Used in Screening Tests

Chemical	K_{oc} Mean	$C_V\%$	Number of soils	Reference	Comments
Atrazine	163	49	56	*55*	Review article
Bromacil	72	102	2	*55*	
Carbofuran	29	30	5	*55*	
2,4–D	20	72	9	*55*	Acid
DDT	243,120	65	2	*55*	
Diazinon	850	—	—	*55*	Calculated[a] from K_{ow}
Dieldrin	12,090	—	—	*55*	Calculated[a] from K_{ow}
Diuron	383	72	84	*55*	
EPTC	283	19	3	*28*	Review article
Ethoprophos	122	32	4	*42*	
Lindane	1300	16	7	*55*	
Methyl parathion	5100	114	7	*55*	
Monuron	184	61	18	*55*	
Napropamide	296	—	1	*19*	0.75% organic matter
Parathion	10,650	75	4	*55*	
Phorate	660	—	—	*55*	Calculated from K_{ow}
Prometryne	614	99	38	*55*	
Simazine	138	13	147	*55*	
Triallate	3600	24	2	*34*	
Trifluralin	7340	—	5	*23*	

[a] Using Eq. (3).

were assigned a single value for all pesticides in cases where we felt that variations among pesticides would not be significant, such as with air diffusion coefficients and water diffusion coefficients. The soil properties of porosity and bulk density, along with relative humidity and temperature, were simply given specified values to provide a common background for all chemicals. Other variables, such as organic carbon fraction, water content, depth of incorporation, and water evaporation rate, are varied in different screening tests to illustrate the sensitivity of different pesticides to variations of such parameters.

VI. RESULTS OF SCREENING TESTS

A. Volatilization

1. Cumulative Losses

Table VI shows 30-day cumulative volatilization for the screening test in which water evaporation did not occur. In this series of simulations,

TABLE IV

Degradation Half-Lives for Pesticides Used in Screening Tests

Chemical	Half-life (days)	Reference	Comments
Atrazine	71	*47*	Mean of four soils; review article
Bromacil	350	*55*	Field experiment; review article
Carbofuran	40	*55*	
2,4–D	15	*55*	Lab data
DDT	3837	*26*	Lab data; review article
Diazinon	32	*55*	
Dieldrin	868	*47*	
Diuron	328	*55*	
EPTC	30	*47*	
Ethoprophos	50	*42*	Lab data
Lindane	266	*55*	
Methyl parathion	15	*55*	
Monuron	166	*26*	
Napropamide	70	*33*	Herbicide handbook
Parathion	18	*55*	Field data
Phorate	82	*55*	
Prometryne	60	*72*	Review article
Simazine	75	*55*	
Triallate	100	*33*	
Trifluralin	132	*55*	

TABLE V

Common Properties Assumed for All Pesticides and Soil in Simulations

	Property	Value
D_G^{air}	Air diffusion coefficient	4320 cm^2/day
D_L^{water}	Water diffusion coefficient	0.432 cm^2/day
ϕ	Porosity	0.5
ρ_b	Bulk density	1.35 g/cm^3
R.H.	Atmospheric relative humidity	0.5 (50%)
T	Temperature	25°C
f_{oc}	Organic carbon fraction	0.0125, 0.025
θ	Water content	0.15, 0.30, 0.45
M	Amount of pesticide applied	1 kg/ha
L	Depth of incorporation	1, 10 cm
E	Water evaporation rate	0, 0.25, 0.50 cm/day
J	Leaching rate	1.0 cm/day

TABLE VI

Cumulative Pesticide Volatilization after 30 Days without Evaporation of Water as a Function of f_{oc}, L (cm), and d (mm), Expressed as a Percentage of Amount Applied[a]

	$L = 1$				$L = 10$			
	$f_{oc} = 0.0125$		$f_{oc} = 0.0250$		$f_{oc} = 0.0125$		$f_{oc} = 0.0250$	
Chemical	$d = 4.75$	$d = 0.475$	$d = 4.75$	$d = 0.475$	$d = 4.75$	$d = 0.475$	$d = 4.75$	$d = 0.475$
Atrazine	1.5	12.7	0.9	7.9	0.2	1.6	0.1	0.9
Bromacil	—	0.4	—	0.3	—	0.1	—	—
Carbofuran	4.5	30.3	3.3	23.8	0.8	5.5	0.5	3.7
2,4-D	0.1	0.7	0.1	0.5	—	0.1	—	0.1
DDT	3.6	4.4	2.3	3.1	0.4	0.4	0.2	0.3
Diazinon	22.7	31.0	14.5	22.1	2.3	3.2	1.4	2.2
Dieldrin	12.6	14.0	8.5	9.9	1.3	1.4	0.9	1.0
Diuron	0.1	1.4	0.1	0.8	—	0.2	—	0.1
EPTC	55.1	56.4	45.2	46.7	7.2	7.4	5.1	5.3
Ethoprophos	27.0	55.7	18.5	45.6	3.5	7.6	2.1	5.4
Lindane	28.4	32.6	19.1	23.2	2.9	3.3	1.9	2.3
Methyl parathion	0.7	4.5	0.3	2.5	0.1	0.4	—	0.3
Monuron	—	0.4	—	0.3	—	0.1	—	—
Napropamide	3.0	20.6	1.7	12.7	0.3	2.3	0.2	1.3
Parathion	0.5	3.3	0.3	1.9	0.1	0.3	—	0.2
Phorate	42.4	44.6	31.3	33.6	4.6	4.8	3.2	3.4
Prometryne	1.1	9.3	0.6	5.1	0.1	1.0	0.1	0.5
Simazine	0.2	2.3	0.1	1.4	—	0.3	—	0.2
Triallate	24.0	25.4	16.6	17.9	2.4	2.5	1.7	1.8
Trifluralin	37.6	38.5	27.0	27.9	4.2	4.0	2.7	2.8

[a] $\theta = 0.3$, $M_0 = 1$ kg/ha.

the organic carbon fractions were 0.0125 and 0.0250, and the depths of incorporation were 1 and 10 cm. In all simulations, 1 kg/ha was added and the water content was uniformly 0.3. Results are shown for specified boundary layers of d = 4.75 mm and d = 0.475 mm. The thinner boundary layer was put in to determine which pesticides were sensitive to changes in d, and also to represent a practical upper limit to the volatilization rate.

Several results are obvious from this table. First of all, for both large and small d, cumulative volatilization loss is related to vapor pressure. Thus, the chemicals with the highest vapor pressure (trifluralin, triallate, phorate, ethoprophos, lindane, EPTC, diazinon) also have the highest volatilization without evaporation. Second, for many chemicals there is a significant increase in volatilization loss when the boundary layer thickness is decreased by a factor of 10, whereas for others—for example, DDT and trifluralin, little or no difference is found. These latter chemicals have volatilization rates that are limited by diffusion to the soil surface and not by diffusion through the boundary layer.

Table VII shows the results of simultaneous volatilization occurring with water evaporation for conditions similar to those in Table VI. In these simulations Eq. (28) is used to calculate the boundary layer thickness for a given evaporation rate.

2. *Rate of Volatilization*

a. Influence of Soil and Management Variables. In Table VII we see a number of differences in the cumulative volatilization losses among chemicals. Some chemicals, such as bromacil, 2,4-D, parathion, methyl parathion, diuron, simazine, and monuron, have small volatilization losses under all conditions. Other chemicals, such as atrazine, napropamide, and ethoprophos, have significantly higher losses with than without water evaporation. A third group of chemicals, including triallate, trifluralin, and dieldrin, seem to be relatively unaffected by water evaporation, but still have high volatilization rates. Figure 1 illustrates this difference in dependence on evaporation by plotting volatilization flux as a function of time for each of the chemicals with 0, 2.5, or 5.0 mm/day of water evaporation (d = 4.75, 4.75, 2.375 mm, respectively) occurring under the same conditions as in Table VII. Here we see that not only the amount of volatilization but even the shape of the volatilization curve with time are different for different chemicals. Volatilization rates for those chemicals that seem to be least affected by changes in evaporation rate decrease monotonically as a function of time, whereas others remain constant or even increase with time.

TABLE VII

Cumulative Pesticide Volatilization after 30 Days with Evaporation E as a Function of f_{oc}, L (cm), and E (mm/day), Expressed as a Percentage of Amount Applied[a]

	$L = 1$				$L = 10$			
	$f_{oc} = 0.0125$		$f_{oc} = 0.0250$		$f_{oc} = 0.0125$		$f_{oc} = 0.0250$	
Chemical	$E = 2.5$	$E = 5.0$	$E = 2.5$	$E = 5.0$	$E = 2.5$	$E = 5.0$	$E = 2.5$	$E = 5.0$
Atrazine	6.4	23.5	3.1	12.2	1.2	6.8	0.4	2.2
Bromacil	0.2	1.0	0.1	0.5	0.1	0.5	—	0.2
Carbofuran	26.5	66.9	17.2	51.1	13.6	53.6	5.9	31.8
2,4-D	0.4	1.8	0.1	0.7	0.2	1.2	0.1	0.7
DDT	3.7	4.2	2.4	2.8	0.4	0.4	0.2	0.3
Diazinon	41.5	65.4	23.8	41.1	4.4	7.9	2.4	4.2
Dieldrin	14.5	17.3	9.4	11.1	1.4	1.7	0.9	1.1
Diuron	0.5	2.0	0.2	0.9	0.1	0.3	—	—
EPTC	76.4	86.1	63.4	77.1	14.0	23.0	8.4	12.8
Ethoprophos	74.0	92.5	52.3	86.4	18.7	47.2	8.4	23.4
Lindane	45.9	67.6	27.9	41.3	4.7	7.4	2.8	4.2
Methyl parathion	1.0	2.6	0.5	1.1	0.1	0.3	—	0.1
Monuron	0.2	0.7	0.1	0.4	—	0.2	—	0.1
Napropamide	10.4	35.9	4.8	18.0	4.4	7.0	0.5	2.3
Parathion	0.7	1.6	0.3	0.7	0.1	0.2	—	0.1
Phorate	66.0	83.8	46.6	64.0	8.1	12.9	4.9	7.1
Prometryne	3.2	12.4	1.3	5.0	0.4	1.6	0.1	0.5
Simazine	0.5	0.9	0.4	0.9	0.2	0.6	0.1	0.4
Triallate	29.9	37.4	19.5	23.5	3.0	3.8	2.0	2.3
Trifluralin	40.1	43.2	28.4	30.3	4.2	4.5	2.9	3.0

[a] $\theta = 0.3$, $M_0 = 1$ kg/ha.

The dependence of volatilization rate on thickness d of the diffusion boundary layer is shown in Fig. 2 under conditions otherwise similar to those in Table VII. The evaporation rate is assumed to be 2.5 mm/day, which according to Eq. (28) is associated with a thickness of 4.75 mm. Also shown in this figure are volatilization rates for diffusion layer thicknesses of 0.475 and 47.5 mm. Wide variations in dependence on this diffusion layer thickness between chemicals are illustrated in this figure. Again, those chemicals whose volatilization rates decrease monotonically, such as EPTC, trifluralin, and phorate, have considerably less dependence upon diffusion thickness, indicating that the volatilization rate is controlled by movement to the soil surface. Others, such as atrazine, napropamide, prometryne, and simazine, are boundary-layer controlled, and have losses that are essentially proportional to the diffusion thickness. Still other chemicals, such as ethoprophos, diazinon, and lindane, seem to undergo

f_{oc}, L (cm),

	= 0.0250
2.5	E = 5.0
4	2.2
.	0.2
)	31.8
1	0.7
2	0.3
4	4.2
9	1.1
–	—
4	12.8
4	23.4
8	4.2
–	0.1
–	0.1
.5	2.3
–	0.1
.9	7.1
.1	0.5
.1	0.4
.0	2.3
.9	3.0

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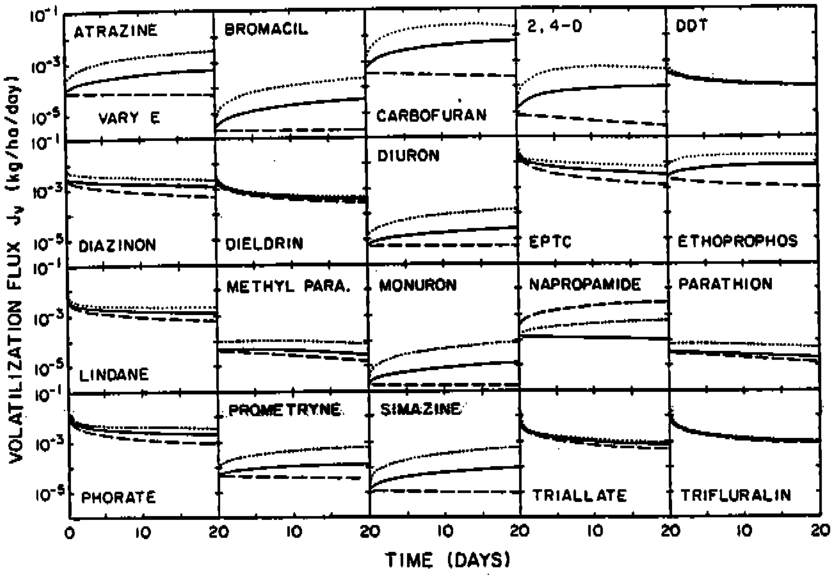

Fig. 1. Volatilization flux versus time for $E = 0$ (dashed line), $E = 2.5$ mm/day (solid line), and $E = 5.0$ mm/day (dotted line), with $L = 10$ cm, $\theta = 0.3$, $f_{oc} = 0.0125$, and $d = 4.75$, 4.75, and 2.375 mm, respectively.

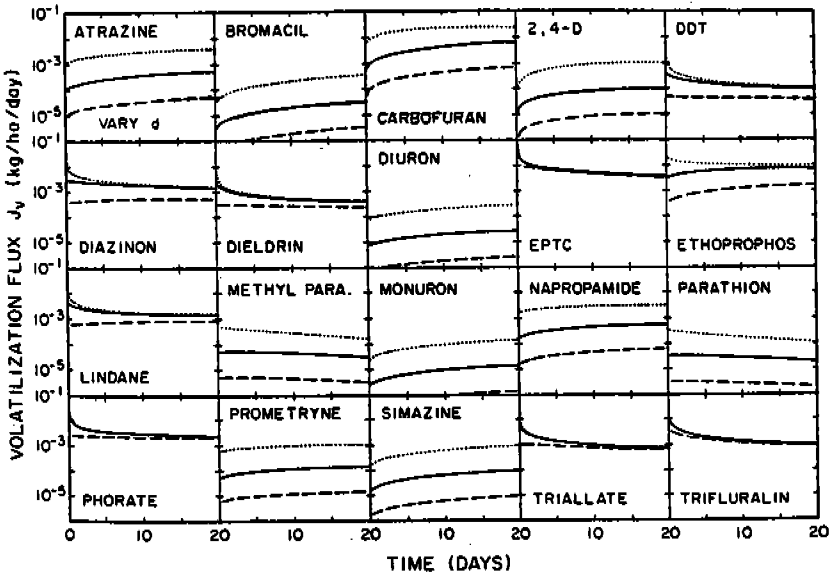

Fig. 2. Volatilization flux versus time as a function of boundary layer thickness for $d = 47.5$ mm (dashed line), $d = 4.75$ mm (solid line), and $d = 0.475$ mm (dotted line), with $L = 10$ cm, $\theta = 0.3$, $f_{oc} = 0.0125$, $E = 2.5$ mm/day.

a transition in behavior as the diffusion thickness is varied over two orders of magnitude.

The dependence of volatilization rate on water content is shown in Fig. 3 for an evaporation rate of 2.5 mm/day and conditions otherwise equal to those in the earlier figures. Significant differences are found in the absolute loss rate of these chemicals and also in their dependence on water content. For those chemicals whose volatilization rates are not controlled by the boundary layer, the dependence is rather moderate, whereas for the boundary-layer controlled chemicals, such as atrazine and simazine, enormous differences are found for different water contents. These results will be discussed in more detail later.

As shown in Tables VI and VIII, the volatilization rates of all chemicals significantly increase when the depth of incorporation is reduced from 10 to 1 cm. The major mechanism responsible for this increase is simply the increase in concentration of the chemical, since a uniform amount is applied. A secondary effect, particularly for those chemicals that lose a substantial fraction of their mass to volatilization, is the decreased distance to the volatilization surface. Figure 4 shows volatilization rates for incorporation depths of 2, 6, and 10 cm for 1 kg/ha applications of

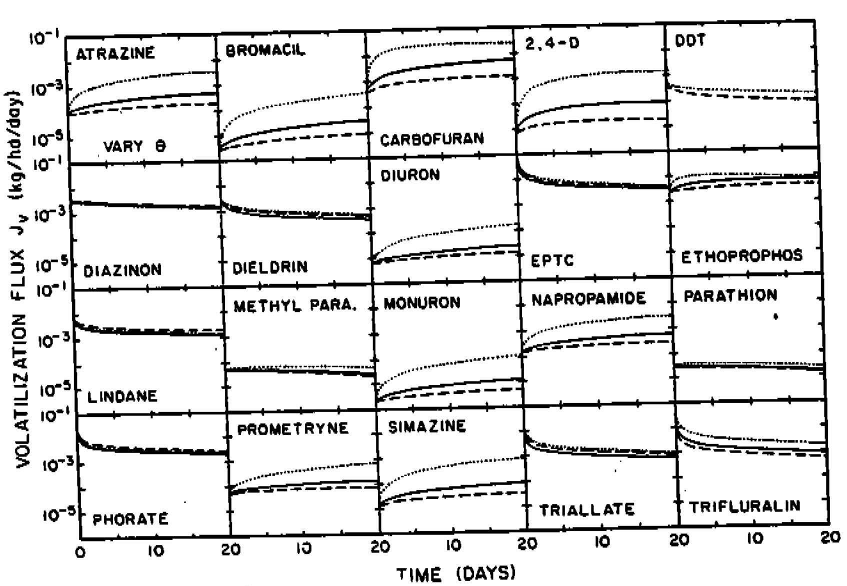

Fig. 3. Volatilization flux versus time as a function of water content for $\theta = 0.15$ (dotted line), $\theta = 0.30$ (solid line), and $\theta = 0.45$ (dashed line), with $L = 10$ cm, $f_{oc} = 0.0125$, $E = 2.5$ mm/day, and $d = 4.75$ mm.

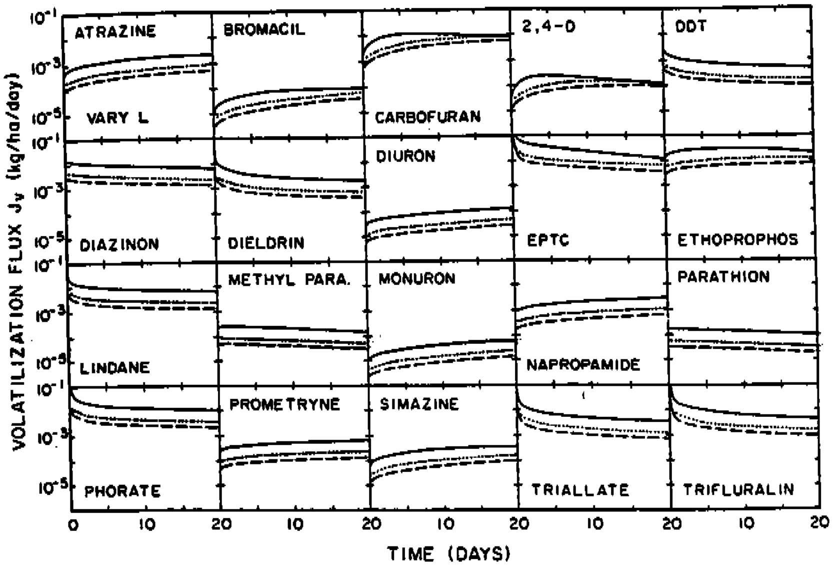

Fig. 4. Volatilization flux versus time as a function of depth of incorporation for L = 2 cm (solid line), L = 6 cm (dotted line), and L = 10 cm (dashed line), with θ = 0.30, f_{oc} = 0.0124, E = 2.5 mm/day, and d = 4.75 mm.

all chemicals. Since the concentration is inversely proportional to the depth of incorporation, the ratio of these initial concentrations (5, 1.67, and 1 mg/liter) roughly explains all features of the graph. The convergence of flux rates at large time for carbofuran and 2,4-D is due to the attainment of saturated vapor densities as concentrations build up because of convective upward flow to the surface and boundary-layer controlled flux to the atmosphere.

b. Sensitivity Analysis. The calculated volatilization rate for each of these chemicals depends in a complex way on the benchmark properties given in Tables I through IV. Since this information is frequently uncertain, we show in Fig. 5, 6, and 7, respectively, the influence of changes in Henry's law constant K_H, organic carbon partition coefficient K_{oc}, and half-life $T_{1/2}$, with conditions otherwise equal to those in earlier calculations (i.e., f_{oc} = 0.0125, θ = 0.30, E = 2.5 mm/day, L = 10 cm, d = 4.75 mm). In these simulations, the variable being studied is changed to 1/3 (dotted line) and 3 (dashed line) times its base value (solid line). It is clear that the volatilizations of some chemicals have significant sensitivity to variations in parameters about which little information may be available.

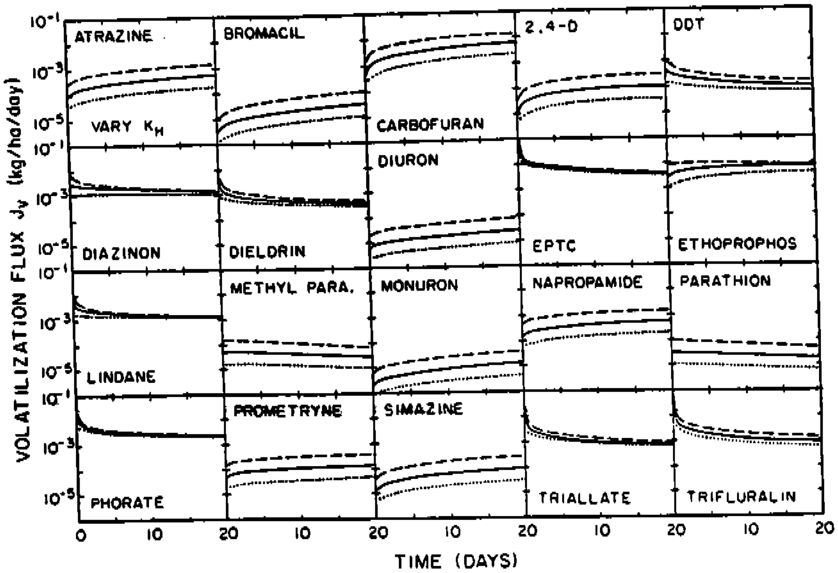

Fig. 5. Sensitivity of volatilization flux versus time to variations in K_H, using base values of K_H (solid line), $3K_H$ (dashed line), and $K_H/3$ (dotted line), with L = 10 cm, θ = 0.30, f_{oc} = 0.0125, E = 2.5 mm/day, d = 4.75 mm.

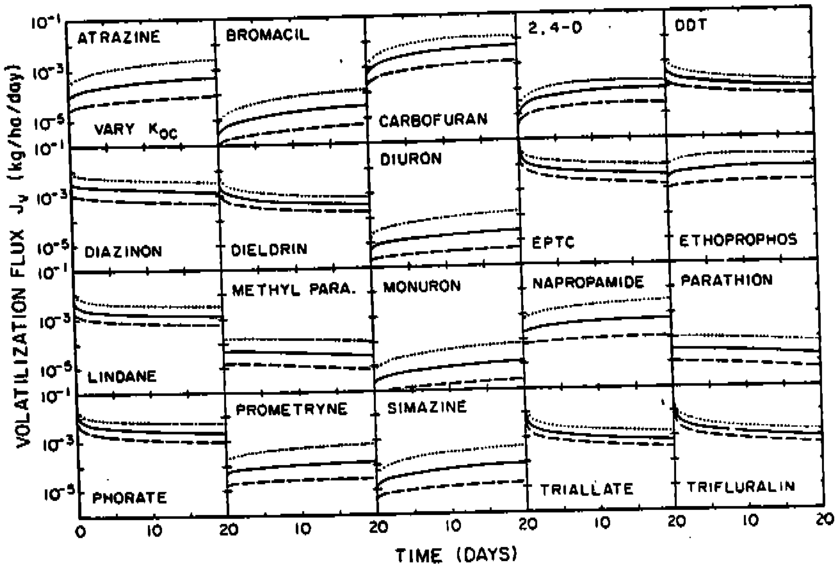

Fig. 6. Sensitivity of volatilization flux versus time to variations in K_{oc}, using base values of K_{oc} (solid line), $3K_{oc}$ (dashed line), and $K_{oc}/3$ (dotted line), with L = 10 cm, θ = 0.30, f_{oc} = 0.0125, E = 2.5 mm/day, d = 4.75 mm.

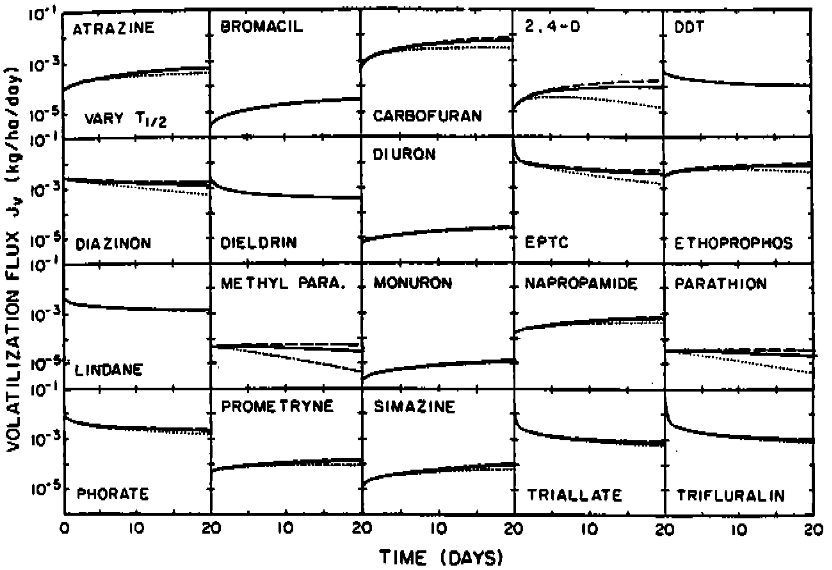

Fig. 7. Sensitivity of volatilization flux versus time to variations in $T_{1/2}$, using base values of $T_{1/2}$ (solid line), $3T_{1/2}$ (dashed line), and $T_{1/2}/3$ (dotted line), with L = 10 cm, θ = 0.30, f_{oc} = 0.0125, E = 2.5 mm/day, d = 4.75 mm.

Thus, the degree of confidence one could have in even qualitative estimates using this model is dependent on the accuracy of the benchmark properties.

B. Persistence

Table VIII shows the calculated fraction of initial mass remaining after 30 days as a function of depth of incorporation and evaporation rate, assuming f_{oc} = 0.0125. The two pathways of loss depleting the mass are degradation and volatilization. Since degradation of each chemical is reasonably constant in different cases, the major differences for a single chemical represent losses due to volatilization, as shown in earlier tables. Thus, volatilization may influence the categorization of pesticide persistence. For example, if we chose a consistent but somewhat arbitrary persistence classification scheme and examined the column in Table VIII corresponding to 5.0 mm/day evaporation and 1 cm incorporation depth, we would classify the 20 pesticides as shown in Table IX. If, however, we used the same classification scheme but looked at the column in Table VIII corresponding to a depth of incorporation of 10 cm, the classifications would change to those shown in Table X. Actual $T_{1/2}$ values from Table

TABLE VIII

Percentage Mass Remaining in Soil after 30 Days as a Function of E (mm/day) and L (cm)[a]

	$L = 1$			$L = 10$		
Chemical	$E = 0.0$	$E = 2.5$	$E = 5.0$	$E = 0.0$	$E = 2.5$	$E = 5.0$
Atrazine	73.6	69.4	54.6	74.7	73.9	68.8
Bromacil	94.3	94.1	93.3	94.3	94.2	93.8
Carbofuran	56.6	39.8	11.6	59.3	48.7	17.9
2,4-D	25.4	25.3	24.6	25.5	25.3	24.8
DDT	95.9	95.8	95.3	99.1	99.1	99.0
Diazinon	37.4	24.0	8.6	51.1	50.0	47.1
Dieldrin	85.2	83.4	80.6	96.4	96.2	95.9
Diuron	93.8	93.5	91.9	93.9	93.9	93.6
EPTC	17.9	5.6	1.9	45.9	41.1	34.7
Ethoprophos	45.4	9.3	0.6	63.5	50.8	27.6
Lindane	65.5	48.6	27.9	89.8	88.0	85.4
Methyl parathion	25.2	25.0	24.1	25.4	25.4	25.3
Monuron	88.3	88.2	87.7	88.4	88.3	88.2
Napropamide	72.0	65.5	43.5	74.3	73.3	68.3
Parathion	31.7	31.6	31.1	32.0	32.0	31.9
Phorate	42.1	21.8	7.3	74.0	70.9	66.6
Prometryne	70.1	68.3	60.4	70.9	70.7	69.7
Simazine	75.9	75.1	72.2	76.0	75.9	74.8
Triallate	60.4	55.1	48.4	79.3	78.8	78.1
Trifluralin	51.7	49.4	46.6	82.1	81.8	81.5

[a] $\theta = 0.3$, $M_0 = 1$ kg/ha, $f_{oc} = 0.0125$.

IV are shown for comparison. Many of the pesticides change categories between these two tables, even though the environmental conditions other than incorporation depth were equivalent.

To illustrate how volatilization might be associated with "persistence" as measured by loss rate, we ran 5-day simulations of pesticide volatilization with accompanying water evaporation of 5.0 mm/day, but with the degradation rate constant of each pesticide set equal to 0 (infinite half-life). Equation (6) was then used to calculate a volatilization degradation constant μ, which is translated into a half-life in Table XI. A number of the chemicals have volatilization half-lives that are comparable to the published half-lives, particularly when the shallow depth of incorporation is used. This suggests that since a number of measurements of half-life have been obtained by measuring differences between initial and final concentrations, volatilization may have appreciably influenced experimental measurements of this quantity.

TABLE IX

Persistence Categories Classified in Terms of Remaining Mass after 30 Days[a]

Fraction of mass remaining (%)	Category	Chemical	Actual $T_{1/2}$[b]
>90	Highly persistent	DDT	3837
		Bromacil	350
		Diuron	328
90 to 60	Persistent	Monuron	166
		Dieldrin	868
		Simazine	75
		Prometryne	60
60 to 30	Moderate	Atrazine	71
		Triallate	100
		Trifluralin	132
		Napropamide	70
		Parathion	18
30 to 10	Short residence time	Lindane	266
		2,4-D	15
		Methyl parathion	15
		Carbofuran	40
<10	Very short residence time	Diazinon	32
		Phorate	82
		EPTC	30
		Ethoprophos	50

[a] $f_{oc} = 0.0125$, $E = 5.0$ mm/day for $L = 1$ cm.

[b] From Table IV.

C. Leaching

Figure 8 shows the peak height and position of the center of mass after 30 days of continuous leaching at 1 cm per day, calculated when the chemical is given a uniform initial incorporation to the 10 cm depth. We have presented only the height and center of the pulses in order to place all chemicals on the same graph. These simulations have two significant features: depth of leaching and height of remaining pulse. The former is influenced most strongly by organic carbon partition coefficient and the latter by degradation rate. Thus, knowledge of the organic carbon partition coefficient or some other index of relative mobility, such as the R_F value obtained through thin-layer chromatography (*32*), is sufficient to establish the susceptibility to leaching of different chemicals.

TABLE X

Persistence Categories Classified in Terms of Remaining Mass after 30 Days[a]

Fraction of mass remaining (%)	Category	Chemical	Actual $T_{1/2}$[b]
>90	Highly persistent	DDT	3837
		Dieldrin	868
		Bromacil	350
		Diuron	328
90 to 60	Persistent	Monuron	166
		Lindane	266
		Trifluralin	132
		Triallate	100
		Simazine	75
		Prometryne	60
		Atrazine	71
		Napropamide	70
		Phorate	82
60 to 30	Moderate	Diazinon	32
		EPTC	30
		Parathion	18
30 to 10	Short residence time	Ethoprophos	50
		Methyl parathion	15
		2,4–D	15
		Carbofuran	40
<10	Very short residence time	None	

[a] $f_{oc} = 0.0125$, $E = 5.0$ mm/day for $L = 10$cm.
[b] From Table IV.

VII. DISCUSSION

In most of the screening tests involving scenarios in which a number of variables are present, the dependence of volatilization, persistence, and leaching on these variables was reasonable. However, as mentioned in the previous section, the chemicals divided roughly into three classes with respect to volatilization losses. Usually, the volatilization fluxes were either highest at time 0 and decreased with time, or they increased with time. The former case corresponds to the situation in which chemicals at the surface are depleted and remain at a low concentration, and the latter case corresponds to the situation in which the concentrations at the surface increase with time. A third class of chemicals displayed behavior intermediate between these two extremes.

TABLE XI

Volatilization Half-Life (Days) Calculated by Assuming Zero Degradation Rate and Calculating $T_{1/2}$ from Residual Mass at t = 5 Days[a]

Chemical	$T_{1/2}$ (L = 1 cm)	$T_{1/2}$ (L = 10 cm)	Actual $T_{1/2}$[b]
Atrazine	97	909	71
Bromacil	2462	17,490	350
Carbofuran	14	68	40
2,4-D	660	2603	15
DDT	247	2487	3837
Diazinon	15	166	32
Dieldrin	61	626	868
Diuron	1918	19,137	328
EPTC	3.7	50	30
Ethoprophos	3.8	46	50
Lindane	18	194	266
Methyl parathion	563	5644	15
Monuron	3965	37,463	166
Napropamide	76	766	70
Parathion	920	9217	18
Phorate	9	105	82
Prometryne	276	2781	60
Simazine	558	4978	75
Triallate	26	281	100
Trifluralin	18	201	132

[a] f_{oc} = 0.0125, θ = 0.3, E = 5.0 mm/day.

[b] From Table IV.

Insight into this phenomena can be found by examining Fig. 9, which shows schematically the influence of the stagnant boundary layer on the volatilization loss during water evaporation. When water evaporation occurs, pesticide is moved toward the soil surface by convection and diffusion, whereas the loss at the surface occurs at a rate $D_G^{air}C_G(0)/d$ [Eq. (21)]. If the vapor flux through the boundary layer is able to match the diffusive and convective flux upward to the soil surface without the surface concentration building up substantially, then the soil flux, and not the boundary layer, controls the volatilization rate. For these chemicals, (e.g., EPTC in Fig. 2) the dependence on boundary layer thickness d will not be significant. Furthermore, if for these chemicals the convective flux J_WC_L is small compared to the diffusive flux, which occurs when K_H or K_{oc} is large, then the dependence of volatilization rate on evaporation rate will not be significant (e.g., DDT, dieldrin, trifluralin in Fig. 1). Conversely, if the diffusion rate through the boundary layer is less than the rate of upward convection and diffusion, then chemicals will tend

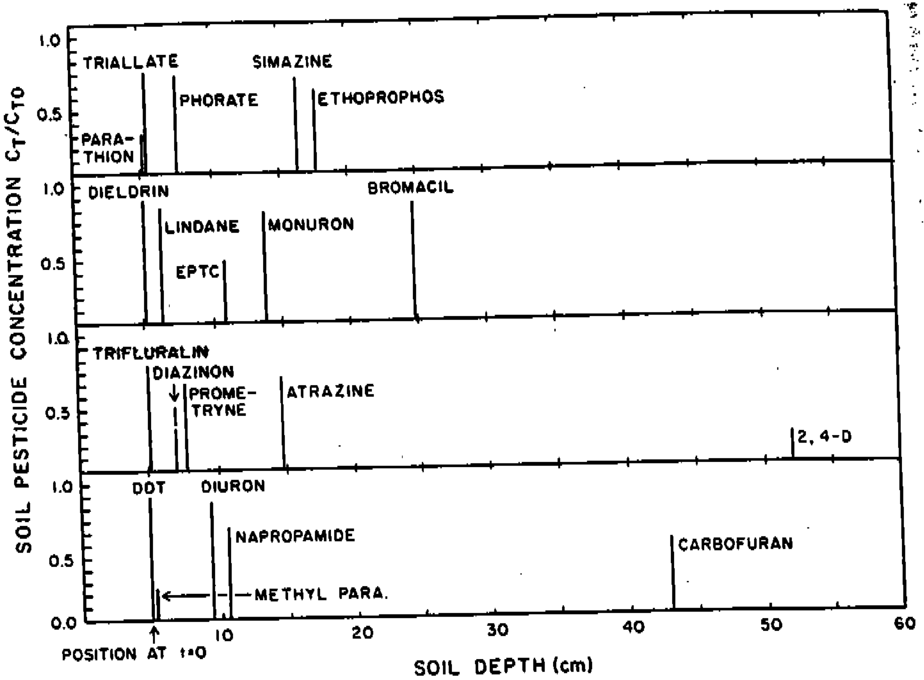

Fig. 8. Position and height of center of pulse of chemical after 30 days of leaching at $J = 1$ cm/day, with $L = 10$ cm, $\theta = 0.30$, $f_{oc} = 0.0125$.

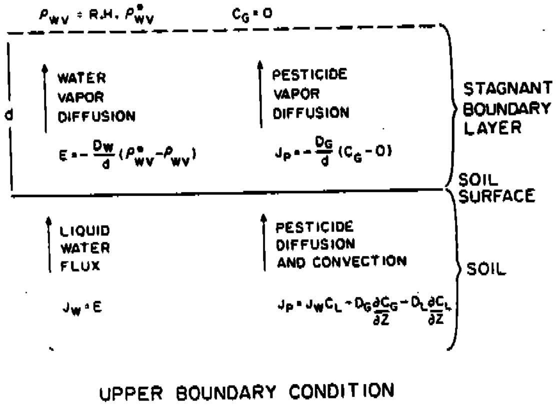

Fig. 9. Schematic diagram of soil surface–boundary layer fluxes of water and pesticide.

to accumulate at the surface. For these chemicals (e.g., atrazine in Figs. 1 and 2), evaporation of water and thickness of boundary layer have a significant effect on volatilization.

It is useful to examine the relative size of the upward soil and boundary layer fluxes when the phase concentrations are at their initial value. We may establish a criterion for identifying which chemicals are boundary-layer controlled by requiring that the convective flux be large compared with the flux through the stagnant air layer:

$$EC_{\mathrm{L}} >> hC_{\mathrm{G}} \quad \text{or} \quad EC_{\mathrm{T}}/R_{\mathrm{L}} >> D_{\mathrm{G}}^{\mathrm{air}}C_{\mathrm{T}}/dR_{\mathrm{G}} \qquad (32)$$

By plugging in the phase partitioning coefficients, along with the model for diffusion boundary layer thickness [Eq. (28)], and assuming that $D_{\mathrm{G}}^{\mathrm{air}} = 0.05$, $D_{\mathrm{WV}}^{\mathrm{air}} = 0.23$, we obtain the following condition on the Henry's law constant K_{H}:

$$K_{\mathrm{H}} << \frac{D_{\mathrm{WV}}^{\mathrm{air}}\,\rho_{\mathrm{WV}}^{*}\,(1 - \mathrm{R.H.})}{2\rho_{\mathrm{WL}}D_{\mathrm{G}}^{\mathrm{air}}} = 2.65 \times 10^{-5} \qquad (33)$$

This equation, which defines the condition for boundary layer control during evaporation, gives us a criterion for identifying how a pesticide will behave when volatilization occurs with evaporation. Table XII gives the values of the Henry's law constant [Eq. (5)] for each of the 20 pesticides, together with a division into one of three categories, depending on whether K_{H} is much greater than (category I), approximately equal to (category II), or much less than (category III) the value 2.65×10^{-5}. It is clear by looking back at the other figures that those category I pesticides that have K_{H} values considerably greater than the threshold value 2.65×10^{-5} (i.e., DDT, dieldrin, EPTC, phorate, triallate, and trifluralin) all behave similarly in that volatilization rate decreases with time and does not depend strongly on d. Conversely, those chemicals with extremely small K_{H} values (i.e., bromacil, 2,4-D, monuron, diuron, carbofuran, atrazine, prometryne, simazine) fall into the boundary-layer controlled category, in which the chemical builds up at the soil surface over time.

Further classification of the behavior of these pesticides can be made on the basis of total diffusion coefficients [Eq. (18)]. Figure 10 shows a plot of effective vapor, liquid, and total diffusion coefficient divided by organic carbon partition coefficient as a function of water content. Some of the pesticides have essentially no vapor movement, whereas with others vapor movement is dominant except at the highest water contents. The absolute value of the diffusion coefficient at a given water content ranges over orders of magnitude for the different pesticides.

TABLE XII

Henry's Law Constant and Corresponding Volatilization Category of Pesticides Used in Simulations

Chemical	Molecular weight	Henry's law constant	Category
Atrazine	216	2.45×10^{-7}	III
Bromacil	261	3.68×10^{-9}	III
Carbofuran	221	3.13×10^{-7}	III
2,4-D	221	5.00×10^{-9}	III
DDT	355	2.13×10^{-3}	I
Diazinon	305	4.95×10^{-5}	II
Dieldrin	381	6.67×10^{-4}	I
Diuron	233	4.05×10^{-8}	III
EPTC	189	5.95×10^{-4}	I
Ethoprophos	241	6.00×10^{-6}	II
Lindane	291	1.33×10^{-4}	I
Methyl parathion	262	4.39×10^{-6}	II
Monuron	199	6.95×10^{-9}	III
Napropamide	271	7.95×10^{-7}	III
Parathion	290	6.13×10^{-6}	II
Phorate	259	3.10×10^{-4}	I
Prometryne	241	5.63×10^{-7}	III
Simazine	202	3.40×10^{-8}	III
Triallate	305	8.00×10^{-4}	I
Trifluralin	335	6.67×10^{-3}	I

VIII. LIMITATIONS OF SCREENING MODEL

It is important to recognize that the model discussed above is not a simulation model. The imposed conditions given in Table V are far too idealized to represent a field situation, and the assumptions of our model should be kept in mind when interpreting the figures and tables. For example, carbofuran, which possesses only a moderate vapor pressure (Table I), is predicted by the model to have high volatilization losses when upward flow of water is occurring (Table VII). The reason for this result is that carbofuran is both a boundary-layer controlled chemical (Table XII) and is quite mobile (K_{oc} = 29, Table III) and hence has a very large convective flux $J_W C_L$, which rapidly increases the surface concentration and keeps the chemical close to vapor saturation. However, if any water had been added when upward flow was occurring the chemical would have been leached downward and the volatilization losses would have been quite different.

It is also important to recognize that the properties in Tables I through IV may not remain constant in time or with different soil conditions and

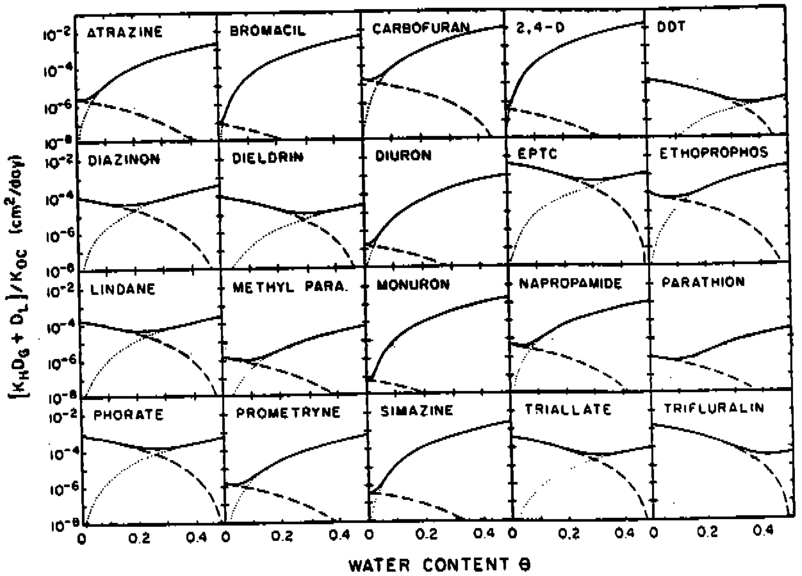

Fig. 10. Calculated vapor (dashed line), liquid (dotted line), and total (solid line) effective diffusion coefficients D_E/f_{oc} as a function of water content θ, using the Millington–Quirk tortuosity model.

that the results given here may change. For example, the choice of benchmark properties for compounds 2,4-D presents special considerations. Several formulations are used in the commercial application of 2,4-D, some of which contain the 2,4-D active ingredient in different chemical forms, each possessing its own set of benchmark properties. For our simulations we used benchmark properties of the acid. This is the chemical form to be expected in many soils following the application of the commonly used low volatile ester formulations of 2,4-D. The 2,4-D esters will rapidly hydrolyze in soil to the acid (*44*, *58*). Obviously, if solubility and vapor pressure values of the ester form of 2,4-D had been used in the simulation, a significantly different picture of its potential volatility and leachability would have resulted—that is, higher volatility and lower leachability. Furthermore, to properly characterize a compound like 2,4-D, consideration would also need to be given to the pH of the soil. In a neutral or high-pH soil, 2,4-D would react with whatever basic cations were present, and the resulting chemical form would have yet another set of benchmark properties. These salts of 2,4-D would be expected to have significantly reduced vapor pressures (*54*).

Finally, chemicals such as 2,4-D illustrate the problems inherent in the selection of the proper half-life. For some compounds whose degradation in soil, like that of 2,4-D, is primarily microbially mediated, the soil microbial population can be preadapted, leading to a much reduced half-life. The half-life of 2,4-D, for example, can be reduced to a matter of hours in cases in which the soil has recently received applications of 2,4-D, as compared to the 15-day half-life estimated by the present simulation for a soil with no prior history of 2,4-D application.

These limitations aside, the model has been shown to be useful not only as a screening tool, but also for sensitivity analysis and for estimating the influence of soil and environmental variables on volatility, mobility, and persistence.

IX. APPLICATION TO OTHER CHEMICALS

In principle, the theoretical model described in Section IV is applicable to any chemical that is present in the soil whose reaction characteristics may be described by the simple first-order expression given in Eq. (6). Thus, not only trace organics but also mobile chemicals such as chloride, or completely gaseous species such as soil oxygen, could be described by the model. In practice it is not the theory but the assumptions that make up the theory which limit its applicability. For example, chemicals that are added to the soil in massive concentrations may not have adsorption isotherms that are well described by the linear expression given in Eq. (1). Furthermore, ionic chemicals that adsorb to mineral surfaces and undergo exchange processes generally have adsorptive properties that depend on other ions in solution as well, a situation not covered by the theory.

Finally, it must be reiterated once more that this is not a simulation model. Therefore, behavior that may be important under field conditions, such as increased adsorption during soil drying, is not taken into account by the model. Our model seeks merely to describe the behavior of one chemical relative to another under a standard prescribed set of conditions.

X. SUMMARY AND CONCLUSIONS

The model calculations have shown that pesticide volatilization, mobility, and persistence are influenced by a variety of soil, chemical, and management factors. Among the physical–chemical properties of a given compound, we have selected the benchmark properties organic carbon partition coefficient K_{oc}, degradation half-life $T_{1/2}$, and Henry's law constant K_H to characterize the relative behavior of a pesticide in a prespecified set of soil and environmental conditions. In particular, we were able to examine the influence of depth of incorporation L, water content θ, presence or absence of water evaporation E, and thickness of stagnant air boundary layer d on volatilization of pesticides, as well as to determine the sensitivity of volatilization estimates to uncertainties in the measured values of the benchmark properties. Finally, we were able to distinguish between compounds whose volatilization fluxes were limited by upward movement to the soil surface and those that were limited by the boundary layer by looking only at the Henry's law constant K_H. The resulting classification scheme explained many of the differences in volatilization among the pesticides examined.

List of Symbols

a	Volumetric air content (cm^3/cm^3)
d	Diffuse boundary layer thickness (mm)
f_{oc}	Organic carbon fraction
h	Diffuse boundary layer transfer coefficient (mm/day)
z	Space coordinate (cm)
t	Time coordinate (days)
C_G	Soil gas concentration ($\mu g/cm^3$ soil air)
C_G^*	Saturated vapor density ($\mu g/cm^3$)
C_L	Soil liquid concentration ($\mu g/cm^3$ soil solution)
C_L^*	Solubility ($\mu g/cm^3$)
C_0	Initial total concentration ($\mu g/cm^3$ soil)
C_T	Total soil concentration ($\mu g/cm^3$ soil)
D	Percentage cumulative degradation
D_E	Effective diffusion coefficient (cm^2/day)
D_G	Soil gas diffusion coefficient (cm^2/day)
D_G^{air}	Gas diffusion coefficient in air (cm^2/day)
D_L	Soil liquid diffusion coefficient (cm^2/day)
D_L^{water}	Liquid diffusion coefficient in water (cm^2/day)
E	Evaporation rate (mm/day)
H_E	Effective transfer coefficient (mm/day)
J	Leaching rate (mm/day)
J_S	Soil pesticide flux (μg (cm^2 soil)$^{-1}$ day^{-1})
J_W	Soil water flux (mm/day)
K_D	Solid–liquid partition coefficient (cm^3 solution/gm soil)
K_H	Henry's law constant (cm^3 solution/cm^3 air)

K_{oc}	Organic carbon partition coefficient ((cm^3 solution/g soil)/f_{oc})
K_{ow}	Octanol–water partition coefficient
L	Depth of initial pesticide incorporation (cm)
M	Initial applied mass of pesticide (kg/ha)
R_F	Thin-layer chromatography leaching index
R_G	Ratio of total pesticide mass to mass in gas phase
R_L	Ratio of total pesticide mass to mass in liquid phase
R_S	Ratio of total pesticide mass to mass in adsorbed phase
R.H.	Relative humidity of air above boundary layer
T	Temperature of soil (°C)
$T_{1/2}$	Pesticide degradation half-life (days)
V	Percent cumulative volatilization
V_E	Effective pesticide convective velocity (mm/day)
μ	Degradation rate constant (day^{-1})
ϕ	Soil porosity
ρ_b	Soil bulk density (gm/cm^3)
ρ_{WL}	Liquid water density (gm/cm^3)
ρ_{WV}	Water vapor density (gm/cm^3)
$\dot{\rho}_{WV}$	Saturated water vapor density (gm/cm^3)
θ	Liquid volumetric water content (cm^3/cm^3)

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