

Reviewing Mathematical Models for Pesticide Leaching Studies

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ABSTRACT

Leaching is an unavoidable phenomenon associated with the pesticide applications. Leaching of pesticide does not only indicate the efficiency of a pesticide molecule, but also degree of the environmental contamination. Leaching is the process by which a pesticide molecule enters the soil-water ecosystem. Hence, to access the leaching behavior of a pesticide molecule, various models are used globally. This paper reviewed some globally adapted leaching models and tried to find the best fitted model for leaching study.

Keywords: Pesticide, leaching, model

The perfect pesticide is applied without losses to target sites, kills or disrupts the target pest only, then disappears. Unfortunately, no perfect pesticides exist. Since most pesticides demonstrate biochemical activity in some non-target species, pesticide regulators and scientists are concerned about the potential for off-site transport. The best way to assess off-site transport is through well-designed field studies. But these studies are costly and time consuming and therefore difficult to repeat for the wide variety of environments in which a pesticide may be used. When these data are not available, which is usually the case, another way must be found to simulate reality. Physical models may be constructed and these may, when combined with mathematical models, provide a compromise between pure prediction and field trials.

The process of modeling the leaching of pesticides is simple in concept but complex in execution. Models are physical, conceptual, or mathematical representations of reality. Screening-level models are an appropriate first step for examining pesticide leaching potential, as long as conservative input assumptions are used. They may consist of comparisons of certain mobility and persistence properties with numerical criteria, or they may require pencil, paper, and a hand calculator. At a higher level of sophistication, a wide variety of computer models are available that can quantitatively

simulate pesticide leaching in the aqueous phase. It is important to pick a model that has been validated in more than one study, has good user support, requires an amount of data input appropriate for the application, and has a history of producing results acceptable to scientists and regulatory authorities. Considering these various criteria for acceptability, EPA's PRZM2 model and the German modification, PELMO, would be appropriate for evaluating leaching potential. The GLEAMS, LEACHM, and CALF models are also scientifically acceptable. Thus there are several model available. In this paper we tried to find the best fitted model for a leaching study.

Leaching

The basic equation used to describe solute transport in soil water is a deceptively simple looking differential equation universally referred to as the "convection-dispersion" equation which relates transport of solutes to the mass motion of the water through soil.

"Management" models generally describe pesticide movement in soil water as a chromatography-like "mobile/immobile phase" partitioning. An adsorption-desorption equilibrium constant K_d is defined as,

$$K_d = C_g / C_w \quad \dots(1)$$

where, C_g , (in mg/kg) and C_w , (in mg/L) are equilibrium concentrations in soil and water, when pesticide is partitioned between them in a well-mixed slurry.

The retardation of the pesticide's movement relative to water increases as K_d increases. Instantaneous equilibrium is assumed at all times and the adsorption desorption isotherm is assumed to be linear. More sophisticated descriptions have been used such as non-equilibrium adsorption, irreversible adsorption, and Freundlich isotherm. Predictions of pesticides leaching below the root zone can be altered by an order of magnitude or more if one allows for the possibility of nonlinear adsorption isotherms, i.e., where $K_d = C_g^{1/n} / C_w$.

K_d describes the sorption of a particular pesticide-soil combination. However, nonionic, nonpolar pesticides are mainly adsorbed by soil organic matter and a "soil organic matter adsorption coefficient", usually by K_{oc} can be calculated as follows:

$$K_{oc} = K_d / F_{oc} \quad \dots(2)$$

where, F_{oc} is the fraction of organic carbon in the soil.

Nonpolar pesticides appear, in general, to exhibit the same tendency to adsorb to soil organic matter in any soil and thus to have approximately the same value of K_{oc} in all soils. Thus, one can approximate the K_d for a pesticide in any soil of known F_{oc} if the K_{oc} of the pesticide is known.

Pesticide properties governing leaching

Solubility and sorption to soil organic carbon

The solubility of a pesticide in water effects how it is formulated, how it behaves during application, and how easily it is entrained in runoff or percolation water. It should be mentioned that solubility is not necessarily related to either leaching mobility or runoff mobility. Paraquat, for instance, is quite soluble but extremely soil bound and thus non-leaching. Atrazine is quite insoluble but has a moderate leaching mobility. It is soil sorption as represented by K_d that determines mobility. For nonionic, low-polarity pesticides there is a relationship between solubility and K_{oc} for example,

$$\log K_{oc} = -0.55 \log Sol_w + 3.64 \quad \dots(3)$$

where Sol_w is the water solubility in mg/lit. Similarly, Wauchope, *et al.* (1992) has found the following relationship to hold true for a wide variety of pesticides:

$$K_{oc} = 3000/\sqrt{Sol_w} \quad \dots(4)$$

Persistence

The other property most affecting pesticide loss in water is persistence. During the time after application and before runoff or leaching, a compound must have the persistence, i.e., the ability to withstand environmental degradation, to remain present until the rainfall event occurs. Environmental degradation is the result of a variety of processes (photo decomposition, hydrolysis, microbial breakdown, oxidation/reduction) whose sum adds up to a "lumped" field persistence time - which is usually measured by taking soil samples in time. Generally the expression used to describe the overall result is a simple exponential decay:

$$C_{t_2} = C_{t_1} \exp[-k (t_2 - t_1)] \quad \dots(5)$$

where, C_{t_2} is the concentration at time 2 and C_{t_1} is the concentration at time 1 and k is a rate constant. Simple exponential decay can also be described in terms of a half-life $t_{1/2}$ which is calculated by,

$$t_{1/2} = \ln(2)/k \quad \dots(6)$$

Influence of application methods

An important distinction should be made between those pesticides that are applied to crop foliage (mainly insecticides and fungicides) and those that are applied mainly to soil. Foliar-applied pesticides are generally very short-lived as far as leaching availability because they either (a) are strongly absorbed by foliage or (b) residues left at the surface are extremely exposed to wind and sun. Thus, chlorpyrifos in one experiment had a foliar half-life of one day and a soil half-life of one week.

Formulation

Several reviews indicate that formulation can have a significant effect on losses in runoff or leachate. An extreme example is "gridballs", large pellets of water-soluble herbicides used in forestry: this formulation will lead to very large runoff and leaching concentrations simply because the pesticide can be mobile yet the dissolving pellet remains at

the surface exposed to the runoff stream. Similarly, wettable powders appear to be vulnerable to runoff because they remain at the surface and may be washed off in as particles.

Model uncertainty

Soil parameters

This is the most fundamental type of uncertainty. One critical example of model uncertainty would be the failure to consider macropores in environments containing large numbers of macropores. No widely-available leaching model adequately addresses macropore flow. It has been found that variability in bulk density (ρ) and hydraulic conductivity varies and affect the model. The CV in the organic carbon fraction can be calculated to be 25% - 55% within each of the five soil orders (Inceptisols, Mollisols, Oxisols, Ultisols, and Vertisols) based on the data presented. Field capacity (FC) had an even lower CV.

Pesticide parameters

The most critical pesticide chemistry parameter for leaching assessment is the degradation rate constant. The term "degradation" is used here in its strictest sense, i.e. transformation to products of low toxicity. These products can represent total degradation, e.g., to CO_2 and H_2O or degradation to simple organic molecules possessing no significant toxicity. The reason why uncertainty in the rate constant is so important is that it occurs as an exponential function in all leaching and runoff models.

It is also important to note that k varies with depth as well, usually decreasing significantly with increasing depth. The decrease in k is likely due to the decrease in microbial populations and, indirectly, organic matter. For example, bacterial populations may decrease by four orders of magnitude over the 0 - 1 m depth range. There appears to be less variability in K_{oc} .

Criteria for selecting and evaluating environmental models

Computer simulation models are valuable tools for assessment of the behavior of chemicals in the environment. However, it has to be considered that models never completely reflect reality, but always simplify a chemical's behavior in the environment

or in environmental compartments. Therefore the results obtained by computer models have to be interpreted considering the simplifications of the model.

1. Validation and calibration with experimental data.
2. Appropriateness of model for task at hand.
3. Model availability and user support.
4. Availability of input data.
5. User friendliness.

Classes of Model

Three generic classes of such models can be identified: research, management, and screening.

1. Research models: Experience with inorganic salt and N has shown that research models are the most ambitious and comprehensive in terms of integrating basic processes, but they are often cumbersome in terms of data requirements and computer execution time, or are nearly nontransferable from the developer to other users. The strength of such models is the opportunity they provide to test in an integrated and comprehensive manner our knowledge of the processes affecting pesticide fate in the unsaturated zone.

LEACHMP (leaching estimation and chemistry model-pesticides) constructed by Hutson and Wagenet (1986). LEACHMP consists of several submodels that estimate (i) water flow, (ii) pesticide transport, (iii) pesticide degradation, (iv) water uptake by plant, and (v) potential evapotranspiration.

Water Flow Submodel: The equation for transient vertical soil-water flow, derived from Darcy's law and the equation of continuity, is,

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\theta) \frac{\partial H}{\partial z} \right] - U(z, t) \quad \dots(1)$$

where θ = volumetric water content ($\text{m}^3 \text{m}^{-3}$), $H = h + z$ = hydraulic head (m), h = soil-water matric potential, (m), $K(\theta)$ = water content-dependent hydraulic conductivity (m s^{-1}), U = sink of water lost by transpiration (s^{-1}), and t and z are depth (m) and time (s), respectively.

The retentivity equation proposed by Campbell (1974) is:

$$h = a(\theta / \theta_s)^{-b} \quad \dots(2)$$

where θ_s is volume water content at saturation and a and b are constants. This equation exhibits a discontinuity at $h = a$ and $\theta / \theta_s = 1$ because h must equal zero at saturation. A better representation of retentivity in real soils is made by replacing Eq. (2) with a parabolic function at high potentials (e.g., Clapp and Hornberger, 1978). Hutson (1983) modified Eq. (2) defining a parabolic section expressed in terms of the constants a and b. For the pressure potential range $0 > h > h_v$,

$$h = \frac{a(1 - \theta/\theta_s)^{1/2} (\theta_i/\theta_s)^{-b}}{(1 - \theta_i/\theta_s)^{1/2}} \quad \dots(3)$$

where, h_v , θ_i is the point of intersection of the exponential and parabolic curves. Applying a capillary model to Eq. (2), Campbell (1974) derived,

$$K(\theta) = K_s (\theta/\theta_s)^{2b+2+p} \quad \dots(4)$$

where K_s is the value of $K(\theta)$ at $\theta = \theta_s$ and p is a pore interaction term determined from measured $K(0)$ data. At pressure potentials less than h_v , Eq. (4) becomes,

$$K(h) = K_s (a/h)^{2+(2+p)/b} \quad (\dots)5$$

In this model, Eq. (4) is used when $h > h_v$ and Eq. (5) when $h < h_v$.

Pesticide Movement Submodel

The diffusion-convection equation for a solute (pesticide) that interacts with the soil surface is,

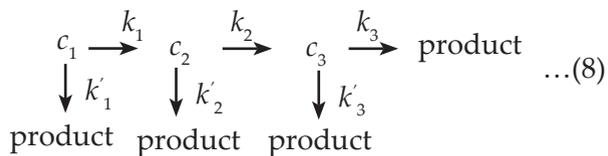
$$\frac{\partial(\theta c)}{\partial t} + \frac{\partial(\phi S)}{\partial t} = \frac{\partial}{\partial z} \left[D(\theta, q) \frac{\partial c}{\partial z} \right] - \frac{\partial(qc)}{\partial z} \pm \phi \quad \dots(6)$$

where, c = pesticide solution concentration ($g L^{-1}$), $\bar{\rho}$ = soil bulk density ($mg m^{-3}$), q = water flux density ($m s^{-1}$), $D(\theta, q)$ = apparent diffusion coefficient ($m^2 s^{-1}$) dependent on θ and q, s = pesticide sorbed concentration ($g kg^{-1}$), and ϕ is a source or sink of pesticide ($g^{-3} d^{-1}$) such as from degradation processes. For most pesticides, sorption reactions are assumed to be sufficiently rapid that local equilibrium exists between dissolved and sorbed forms of the chemical. This has led to a simple linear expression relating solution and sorbed phases,

$$s = K_d c \quad \dots(7)$$

where K_d is the partition or distribution coefficient (kg^{-1}) for the solute.

Pesticides are usually assumed to degrade in soil according to first-order microbiological rate processes. It is often of interest to follow the resulting displacement of daughter products in addition to the original parent compound.



where, c = pesticide concentration, $k_i (s^{-1})$ represents oxidative degradation, and $k'_i (s^{-1})$ represents degradation by hydrolysis. The subscripts on c and k identify different species and the reactions associated with them, with specific pesticide species to be identified below for the example case presented in this study. Expressed as first-order kinetics, Eq. (8) becomes,

$$\begin{aligned} dC_1 / dt &= -(k'_1 + k_1) C_1 \\ dC_2 / dt &= -(k'_2 + k_2) C_2 + k_1 C_1 \\ dC_3 / dt &= -(k'_3 + k_3) C_3 + k_2 C_2 \end{aligned} \quad \dots(9)$$

where, each right-hand side of Eq. (9) is a potential ϕ term in Eq. (6).

2. Management models

The US-EPA model PRZM (Carsel *et al.*, 1984) is a management model of pesticide fate, with commensurately simplified expressions of water flow and solute displacement to reduce input characterization data. PRZM is being widely used throughout the world.

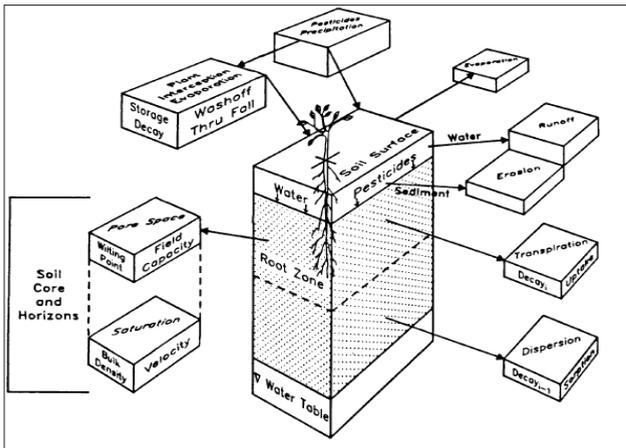
PRZM

The Pesticide Root Zone Model (PRZM) (Carsel *et al.*, 1984, Carsel *et al.*, 1985) was designed and developed as a code for Agency in simulating the transport and transformation of agriculturally applied pesticides in the crop root zone. As such, PRZM attained a degree of acceptability in both the regulatory community and in the agricultural chemical industry. PRZM has two major components– hydrology and chemical transformation and transport.

There were some severe limitations of the PRZM Release I Code:

- (a) Hydrology
- (b) Soil hydraulics

- (c) Method of solution of the transport equation
 (d) Deterministic nature of the model



The capability to simulate soil temperature was added to PRZM-2. The representation of soil hydraulics has been retained in PRZM-3, the user has the option, with the linked modeling system, of coupling PRZM to VADOFT (Vadose Zone Flow and Transport) Model. PRZM-3 is then used to model just the root zone, while VADOFT, with a more rigorous representation of unsaturated flow, is used to simulate the rest of the vadose zone. The description of the processes simulated by PRZM is broken-down in the following discussion into eight categories:

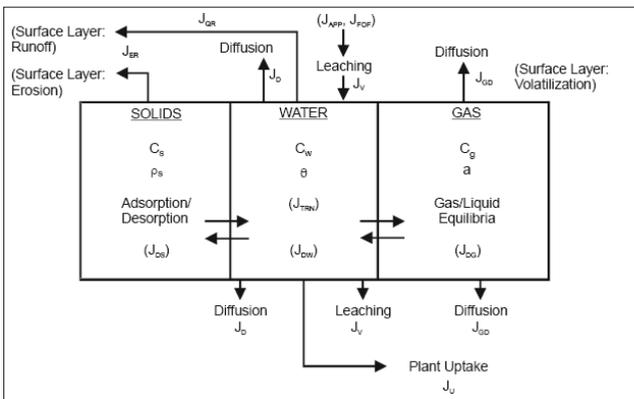
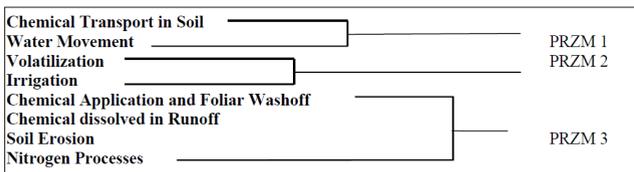


Fig. Schematic representation of a single chemical in a soil layer

Chemical Transport in Soil

The PRZM-3 model was derived from the conceptual, compartmentalized representation of the soil profile as shown. From consideration of, it is possible to write chemical mass balance equations for both the surface and subsurface zones. Addition of the vapor phase and ponded water compartments in PRZM-3 require the consideration of additional terms compared to previous PRZM releases. The surface zone mass balance expressions for each of the dissolved, adsorbed, and vapor phases are:

$$A\Delta z \frac{\partial(C_w \theta)}{\partial t} = J_D - J_V - J_{DW} - J_U - J_{QR} + J_{APP} + J_{FOF} \pm J_{TRN} \quad \dots(6.1)$$

$$A\Delta z \frac{\partial(C_g \rho_g)}{\partial t} = -J_{DS} - J_{ER} \quad \dots(6.2)$$

$$A\Delta z \frac{\partial(C_g a)}{\partial t} = J_{GD} - J_{DG} \quad \dots(6.3)$$

where,

A = cross-sectional area of soil column (cm^2)

Δz = depth dimension of compartment (cm)

C_w = dissolved concentration of pesticide (g cm^{-3})

C_w = dissolved concentration of pesticide (g cm^{-3})

C_s = sorbed concentration of pesticide (g g^{-1})

C_g = gaseous concentration of pesticide (g cm^{-3})

θ = volumetric water content of soil ($\text{cm}^3 \text{cm}^{-3}$)

a = volumetric air content of the soil ($\text{cm}^3 \text{cm}^{-3}$)

ρ_s = soil bulk density (g cm^{-3})

t = time (d)

J_D = represents the effect of dispersion and diffusion of dissolved phase (g day^{-1})

J_V = represents the effect of advection of dissolved phase (g day^{-1})

J_{GD} = represents the effect of dispersion and diffusion in vapor phase (g day^{-1})

J_{DW} = mass loss due to degradation in the dissolved phase (g day^{-1})

J_{DG} = mass loss due to degradation in the vapor phase (g day^{-1})

J_U = mass loss by plant uptake of dissolved phase (g day^{-1})

J_{QR} = mass loss by removal in runoff (g day^{-1})

J_{APP} = mass gain due to pesticide deposition on the soil surface (g day⁻¹)

J_{FOF} = mass gain due to washoff from plants to soil (g day⁻¹)

J_{DS} = mass loss due to degradation of sorbed phase chemical (g day⁻¹)

J_{ER} = mass loss by removal on eroded sediments (g day⁻¹)

J_{TRN} = mass gain or loss due to parent/daughter transformations

Equations for the subsurface zones are identical to Equations 6.1, 6.2, and 6.3 except that J_{QR} , J_{FOF} and J_{ER} are not included. J_{APP} applies to subsurface zones only when the pesticides are incorporated into the soil. For subsurface layers below the root zone, the term J_U is also not utilized.

Dispersion and diffusion in the dissolved phase are combined and are described using Fick's law:

$$J_D = -A\Delta z D_w \frac{\partial^2 (C_w \theta)}{\partial z^2} \quad \dots(6.4)$$

where,

D_w = diffusion-dispersion coefficient for the dissolved phase, assumed constant (cm² day⁻¹)

C_w = dissolved concentration of pesticide (g cm⁻³)

θ = volumetric soil water content (cm³ cm⁻³)

z = soil depth dimension (cm)

The dependence of the molecular diffusivity of the pesticide in air-filled pore space of the volumetric soil air content is described by the Millington-Quirk expression (Jury *et al.*, 1983a).

$$D_2 = \frac{a^{10/3}}{n^2} D_a \quad \dots(6.5)$$

where,

a = the air-filled porosity (cm³ cm⁻³)

ϕ = total porosity (cm³ cm⁻³)

D_a = molecular diffusivity of the chemical in air, assumed constant (cm² day⁻¹)

The advective term for the dissolved phase J_V describes the movement of pesticide in the bulk flow field:

$$J_V = A\Delta z V \frac{\partial (C_w \theta)}{\partial z} \quad \dots(6.6)$$

where,

V = velocity of water movement (cm day⁻¹)

Degradation of a pesticide in or on soil can be due to such processes as hydrolysis, photolysis, and microbial decay. If these processes follow pseudo first-order kinetics, the rate coefficients can be combined into a single, overall or lumped decay coefficient. Assuming the same rate constants for the solid and dissolved phases, the rate of change of chemical out of each phase due to decomposition is given by:

$$J_{DW} = K_s C_w \theta A \Delta z \quad \dots(6.7)$$

$$J_{DS} = K_s C_s \rho_s A \Delta z \quad \dots(6.8)$$

$$J_{DG} = K_g C_g a A \Delta z \quad \dots(6.9)$$

where,

K_s = lumped, first-order decay constant for solid and dissolved phases (day⁻¹)

K_g = lumped, first-order decay constant for vapor phase (day⁻¹)

C_s = solid-phase concentration of pesticide (g g⁻¹)

Summing Equations 6.1, 6.2 & 6.3 the mass balance of pesticide in the uppermost soil layer:

$$\begin{aligned} \frac{\partial}{\partial t} [C_w (\theta + K_d \rho_s + a K_H)] &= -D_w \frac{\partial^2 (C_w \theta)}{\partial z^2} \\ -D_g \frac{\partial}{\partial z^2} (a C_w K_H) - V \frac{\partial}{\partial z} (C_w \theta) \\ -C_w \left[K_s (\theta + K_d \rho_s) + K_g a K_H + f \theta \epsilon + \frac{Q}{A_w \Delta z} + \frac{P X_e r_{om} K_d}{A_w \Delta z} \right] \\ + \frac{J_{APP}}{A \Delta z} + \frac{E P_r M}{\Delta z} - K_{TRN} C_w \theta + \sum_k K_{TRN_k} C_w^k \theta \end{aligned}$$

Because V and θ are not generally known and not generally measured as part of routine monitoring programs, it is necessary to develop additional equations for these variables. In the general case, Darcy's law can be combined with the continuity equation to yield the Richards equation (Richards 1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\theta) \frac{\partial h}{\partial t} \right] \quad \dots(6.10)$$

where,

$K(\theta)$ = hydraulic conductivity at various heads (cm see⁻¹)

θ = soil water content (cm³ cm⁻³)

and,

$$V = -K(\theta) \frac{\partial h}{\partial t} \quad \dots(6.11)$$

Or in simple terms,

$$\frac{\partial \theta}{\partial t} = -\frac{\partial V}{\partial z} \quad \dots(6.12)$$

where, V = soil water velocity (cm day⁻¹)

Writing Equation in an integrated backwards finite difference form yields:

$$\Delta z (\theta^{t+1} - \theta^t) = (V_t - V_{t-1}) \Delta t \quad \dots(6.13)$$

Or

$$\theta^{t+1} \Delta z = (V_t - V_{t-1}) \Delta t + \theta^t \Delta z \quad \dots(6.14)$$

In these equations, t and $t+1$ denote the beginning and end of time step values, respectively, and " I " is the soil layer index. These equations can be simplified by substituting the nomenclature SW for $\theta \Delta z$ so that,

$$SW^{t+1} = SW^t + (V_t - V_{t-1}) \Delta t \quad \dots(6.15)$$

where, SW = soil water content (cm)

Water balance equations are separately developed for (a) the surface zone, (b) horizons comprising the active root zones, and (c) the remaining lower horizons within the unsaturated zone. The equations are:

Surface zones

$$SW_1^{t+1} = (SW)_1^t + INF - I_1 - E_1 - U_1 \quad \dots(6.16)$$

Root zones

$$(SW)_i^{t+1} = (SW)_i^t + I_{i-1} - U_i - I_i \quad \dots(6.17)$$

Below root zones

$$(SW)_i^{t+1} = (SW)_i^t + I_{i-1} - I_i \quad \dots(6.18)$$

where,

$(SW)_i^t$ = soil water in layer " I " on day " t " (cm)

E_i = evaporation (cm day⁻¹)

U_i = transpiration (cm day⁻¹)

I_i = percolation out of zone i (cm day⁻¹)

INF = infiltration into layer 1 (cm day⁻¹)

Infiltration is calculated as:

$$IMF = P + SM - Q - E \quad \dots(6.19)$$

where, assuming unit area 1 cm²

P = precipitation as rainfall, minus crop interception (cm day⁻¹)

SM = snowmelt (cm day⁻¹)

Q = runoff (cm day⁻¹)

E = evaporation (cm day⁻¹)

The calculations of precipitation, snowmelt, and runoff on a daily time step has been considered similarly.

Substantially more simplified models such as MOUSE (Pacinka and Steenhuis, 1984) and CMIS (Nofziger Hornsby, 1984) have been developed to serve broad educational purposes and provide qualitative guidance in pesticide management. In the case of all management models, the ability of the model to quantitatively estimate pesticide fate under field conditions is questionable.

Screening and index models

A number of screening techniques for field run-off or leaching to ground water have been proposed by workers for use as an initial stage (first tier) in evaluating whether pesticides are likely to cause an environmental threat. These screening approaches are based on basic physical-chemical parameters, simple calculations (empirical or analytical solutions), or pre-calculated nomograms (graphs). They are at best semi-quantitative and most useful for predicting very safe or very risky situations.

Screening criteria

EPA criteria

A review of data on the presence of pesticides in ground water from monitoring studies in the USA by Cohen *et al.* (1984).

Pesticide characteristics

- ◆ Water solubility greater than 0 ppm
- ◆ K_d less than 5 (and usually less than 1 or 2)
- ◆ K_{oc} less than 300-500
- ◆ Henry's law constant less than 10⁻² atm-m³/mol
- ◆ Speciation - negatively charged (either fully or partially) at ambient pH.
- ◆ Hydrolysis half-life greater than 25 weeks
- ◆ Photolysis half-life greater than 1 week
- ◆ Soil half-life greater than 2-3 weeks

In addition, the authors had suggested the following set of vulnerable field conditions that may not now be used explicitly by the EPA.

Field Conditions

- ♦ Recharge - total precipitation and irrigation recharge greater than 25 cm/yr. An important factor in this criterion is the soil's drainage ability; i.e. soils with low moisture holding capacity are conducive to high recharge.
- ♦ Nitrates - high levels in the ground water are indicative of pesticide ground water contamination potential.
- ♦ Aquifer - unconfined; porous soil above unconfined aquifer.

Screening-level tier used by Germany, Denmark, and the Netherlands

These three countries estimate and evaluate the ground water contamination potential of pesticides using a three-tiered approach. The first tier is based on to the EPN Cohen, *et al.* criteria described above.

Mobility

- ♦ Water solubility > 30 mg/l
- ♦ Organic carbon sorption constant (K_w) < 500 ml /gm
- ♦ Sorption coefficient (K_d) < 10 ml /gm
Degradability in soil.
- ♦ DT_{50} > 21 days

Indexing models

GUS

The GUS index (or Ground Water Ubiquity Score) is based on a graphical examination of the pesticides found in ground water on a plot formed by two widely available pesticide properties, the half-life in soil ($t_{1/2}$) and the partition coefficient between soil organic carbon and water (K_{oc}). The index is calculated using the empirical equation.

$$GUS = \log(t_{1/2} \text{ soil}) \times (4.0 - (\log K_{oc})) \quad \dots(7)$$

Other physical properties, such as water solubility, octanol-water partition coefficient and volatility from soil, which have often been suggested as indicators of leachability, were not considered to

be useful in discriminating between compounds that did or did not leach. The cutoff ranges of the GUS index are:

- ♦ non-leachers less than 1.8
- ♦ transition range 1.8 - 2.8
- ♦ leachers greater than 2.8

Attenuation Factor - Rao, *et al.* (1985) proposed a quantitative index for screening the potential for pesticides to leach to ground water. The index is called the Attenuation Factor (AF). AF incorporates considerations for pesticide decay and travel time. The latter factor incorporates pesticide retention and water flux. The value of AF is a fraction, the fraction of pesticide lost below the root zone. The equation takes the form:

$$AF = \exp(-B) = M_2 / M_0 \quad \dots(8)$$

where,

M_2 = mass lost below the root zone,

M_0 = amount of pesticide applied to the soil surface,

$B = k(\text{tr})$,

k = degradation rate constant, and

tr = pesticide travel time in the vadose zone.

The travel time tr is calculated by the following equation:

$$\text{tr} = (L)(\text{RF})(\text{FC}) / q \quad \dots(9)$$

where,

L = the depth for calculation,

RF = retardation factor ($1 + q K_d / \theta$),

FC = field capacity, and

q = net recharge rate.

[RF can include a volatilization term as well.]

The Attenuation Factor computation, the GUS index calculation, and the mobility and persistence leaching criteria are used most frequently and appear to be most reliable at the screening level.

PIRI (Pesticide Impact Rating Index)- Pesticide users, natural resource managers, regulators, government agencies and many others are concerned about the off-site impact of pesticides on the environment. Rai S. Kookana, Raymond Correll and Rosalind Miller (1998) have developed a software package named Pesticide Impact Rating Index (PIRI) that outputs an improved pesticide

risk indicator for water quality. PIRI is based on pesticides use, the pathways through which the pesticides are expected to migrate to the water resources (asset), and the value of the asset. Each component is quantified using site conditions (soil type, soil organic matter content, water input, slope of land, soil loss, recharge rate, depth of water table etc.) and environmental conditions (rainfall and temperature).

In PIRI, the detriment is calculated as the product of the three components, i.e.

$$\text{Detriment} = LT V \quad (10)$$

where, L is the pesticide load factor, T the transport factor and V the asset value factor.

Pesticide Load

Since the transport factor depends on the properties of each pesticide (e.g. sorption (K_{oc}) and persistence in the environment (half-life)), the load on the water body has to be considered separately for each pesticide. The calculation of the pesticide load factor requires knowledge of how much of each pesticide is used under each land use in the study area. The load factor (L_i) of a pesticide (p_i) applied in an area is determined from its frequency of application (f_i), dose (d_i) kg m⁻², active ingredient fraction (a_i) in the product and the proportion of the area (p_i) that receives the pesticide:

$$\text{Load}_i = L_i = f_i \times d_i \times a_i \times p_i \quad \dots(11)$$

Pesticide Transport

Transport to Groundwater

PIRI uses a modified version of the Attenuation Factor (AF) index for assessment of the pesticide leaching to the groundwater. The AF index was developed by Rao *et al.* (1985) and has commonly been used in the assessment of groundwater impact of pesticides (Loague and Corwin, 1996). Movement of pesticides through soil is often slower (retarded) than the movement of water due to the sorption of pesticides to soil organic matter, K_{oc} – the higher the K_{oc} , the greater the retardation. The retardation factor, RF, can be measured from K_{oc} and other soil properties by:

$$\text{RF} = \left[1 + \frac{\rho f_{oc} K_{oc}}{\theta_{FC}} \right] \quad \dots(12)$$

where, ρ is the bulk density of soil (kgm⁻³), f_{oc} is the organic carbon content (kg kg⁻¹ soil), and θ_{FC} is the volumetric moisture content of the soil at field capacity (mm⁻³). The rate of water movement in the soil profile can be represented by the quotient of the recharge rate, q , and θ_{FC} . The fraction of pesticide that is lost through degradation will depend on the residence time t in the soil and the decomposition rate. If water enters the soil at a rate of q metres per day, the time required for water to pass through a soil profile of depth D is $D/\text{velocity} = D\theta_{FC}/q$, where D is generally the depth to the water table.

Thus, the residence time of the pesticide in a soil profile of known depth D is,

$$t = \frac{D\theta_{FC}RF}{q} \quad \dots(13)$$

The degradation of a pesticide during its transport through and residence time in the vadose zone (t in Equation (13)) can be represented by the AF for the groundwater, as given by Rao *et al.* (1985), as,

$$\text{AF}_{GW} = \exp \left[\frac{-0693D\theta_{FC}RF}{qt_{1/2}} \right] = \exp \left[-t \frac{(\ln 2)}{t_{1/2}} \right] \quad \dots(14)$$

where $t_{1/2}$ is the half-life of the pesticide in soil.

It is implicit in Equation (14) that both the RF and $t_{1/2}$ of each pesticide remain unchanged throughout the soil profile. However, it is well established that organic carbon content as well as microbial population density and activity decrease significantly with depth in soil profile (Jury *et al.*, 1983; Kookana and Aylmore, 1994; Wilson *et al.*, 1993; Wauchope *et al.*, 2002). These changes need to be incorporated into the index.

Modification to the AF Index

As a modification to the AF index of Rao *et al.* (1985), we have taken into account the decreasing organic carbon (OC) content and microbial population density (MPD) with the soil profile depth. We assumed an exponential decline of OC and MPD with depth as suggested by Jury *et al.* (1983). This decrease in OC with depth has a two-pronged effect on pesticide leaching. Not only does the RF decrease with decreasing OC (and increasing depth) but also the degradation rate of pesticides decreases. The combination of these two components has a significant effect on pesticide leaching. To calculate the effective AF, we follow Jury *et al.* (1983) and

divide the soil profile into three zones: a surface layer with constant OC and MPD, a transition zone with exponentially decreasing OC and MPD and a residual zone with both OC and MPD at a constant residual level. The AF is calculated for the three zones in the profile separately (see below) and the combined attenuation factor is calculated by multiplying these three AF values.

Surface Zone AF (AF_{SZ})

Soil to a depth of 0.1m is well mixed through tillage, and as such it has constant OC and MPD. For this surface zone, AF_{SZ} can be directly calculated using Equation (14), employing the RF based on the organic carbon content of the surface soil and the rate of degradation from the half-life of the pesticide.

Transitional Zone AF (AF_{TZ})

The transitional zone AF is calculated for a depth of 0.1–1.0 m in the soil profile. A range of data on organic matter distribution with depth (e.g. the organic matter of Montana agricultural soils presented by Wilson *et al.*, 1993) indicates that by a depth of 1.0 m, OC is often only about 10% of that of surface soil. It approximates the rate of decline of OC and therefore the rate of degradation of a pesticide ($\mu = \ln 2 / t_{1/2}$) with soil depth by an exponential equation, which has the form,

$$\frac{dy}{dz} = \exp(-k(z - 0.1)) \quad \dots(15)$$

where z is the depth (m) in the transition zone and k a parameter reflecting the rate of decline of f_{oc} and μ with z . A value of 2.98 for k achieves a value of 0.1 at a depth of 1 m.

Residual Zone AF (AF_{RZ})

In the residual zone ($1.0 > z > D$), both f_{oc} and μ are assumed to remain constant to the depth to the groundwater at a level 1/10 of that in the surface zone. The water movement in this zone is appropriately represented by the groundwater recharge rate q . Consequently AF_{RZ} is calculated by using Equation (15) with f_{oc} and μ as 1/10th of those of the surface zone. The net AF for the three zones combined is represented by the following:

$$AF_{GW} = AF_{SZ} \times AF_{TZ} \times AF_{RZ} \quad \dots(16)$$

The expected impact on the groundwater is the product of the load (Equation (11)) and transport (Equation (14)) of each pesticide where AF_{GW} is the transport function T_i of each pesticide. The total load of a pesticide that is likely to reach groundwater at a site is:

$$\text{Groundwater Load} = L_{GW} = \sum L_i AF_{GW_i} = \sum L_i T_i \quad \dots(17)$$

It is assumed that the concentration of a pesticide in the groundwater is a result of the mixing of the pesticide residue in certain thickness of the aquifer (e.g. top 1 m) and soil porosity (θ_s). Assuming top 1 m is the mixing zone in the aquifer (a conservative estimate), the predicted concentration (C_{GW_i} in kgm^{-3}) of pesticide in the top 1 m of the water table is:

$$C_{GW_i} = L_i \times AF_{GW_i} \times \frac{1}{\theta_s} \quad \dots(18)$$

where L_i is the mass of pesticide applied (kg m^{-2}) to the soil (Equation (11)), and θ_s is the porosity of the aquifer.

This concentration (Equation (18)) can be related to the detection limit of the method of analysis in a monitoring programme (Equation (19)). It can also be compared to the acceptable concentration of pesticide in groundwater or surface water, where the acceptable concentration may be represented by parameters such as Drinking Water Standards, Health Advisories (HAL) (USEPA, 2000) or guideline values for drinking water quality (ANZECC, 1997).

$$\text{Groundwater Risk Index} = \frac{C_{GW}}{\text{Detectable or Acceptable concentration}} \quad \dots(19)$$

Transport to the Surface Water: The total surface transport factor for each pesticide is therefore:

$$T = T_{erosion} + T_{direct\ runoff} + T_{drift} \quad \dots(20)$$

Where,

$$T_{Erosion} = a \left(\frac{(\text{Soil Loss Factor}) \times f_2}{1 + \frac{1}{bK_{oc}f_{oc}}} \right) \exp\left(-t \times \frac{\ln 2}{t_{1/2}}\right)$$

$$T_{direct\ runoff} = a \left(\frac{Rf1}{P} \times \frac{1}{1 + f_{oc}K_{oc}} \right) \left(\exp\left(-t \frac{\ln 2}{t_{1/2}}\right) \right)$$

$$T_{drift} = \int_x^{x+w} f_{drift} \text{ (droplet size, distance, width of water body)}$$

Toxicity of the Pesticide to Organisms

The fraction of the applied mass of a pesticide that potentially moves off-site through the various pathways is represented by T in Equation (20). This together with the pesticide load (Equation (11)) provides an estimate of the amount of pesticide moving offsite per unit area (kg m^{-2}), i.e.

$$\text{Pesticide load moving off-site} = (Li) \times Ti \quad \dots(21)$$

Thus the predicted concentration (C_{SW} in kg m^{-3}) of pesticide in surface water with depth H (m), adjacent to treated area is:

$$C_{SW} = L \times T \times \frac{WI}{H} \quad \dots(22)$$

where, WI is the water index defined as an approximate ratio of length of shoreline of the adjacent surface water to the perimeter of the field being treated (OECD, 1998).

Considering the availability of toxicity data, only the acute toxicity data is used as a relative indicator of pesticide toxicity to an organism. Different trophic levels are represented in PIRI. Toxicity to human and animals is covered either through the mammalian toxicity (LD_{50} to rats) or other indicators such as Drinking Water Standards and Health Advisories (USEPA, 2000). The choices of organisms are primarily driven by the availability of ecotoxicological data in the literature.

Surface water Risk Index = C_{SW} /Toxicity Value
(e.g. LC_{50} or EC_{50})

Asset Value Factor

The value of the asset is important when a land use is compared across different water bodies. A subjective scoring system ranging from 1 to 100 is used in PIRI. The water resource used for drinking or of high ecologically value has the highest value (100) and saline water with minimum ecological significance the lowest (one but not zero).

Case study

Accurate input data for leaching models are expensive and difficult to obtain which may lead to the use of "general" non-site-specific input data. This study investigated the effect of using different quality data on model outputs. Three models of

varying complexity, GLEAMS, LEACHM, and HYDRUS-2D, were used to simulate pesticide leaching at a field trial near Hamilton, New Zealand, on an allophonic silt loam using input data of varying quality (Close *et al.*, 2006). Each model was run for four different pesticides (hexazinone, procymidone, picloram and triclopyr); three different sets of pesticide sorption and degradation parameters (i.e., site optimized, laboratory derived, and sourced from the USDA Pesticide Properties Database); and three different sets of soil physical data of varying quality (i.e., site specific, regional database, and particle size distribution data). Models run with pesticide sorption and degradation parameters derived from observed solute concentrations data provided simulation outputs with goodness-of-fit values closest to optimum, followed by laboratory-derived parameters, with the USDA parameters providing the least accurate simulations. Modeling of pesticide movement was performed using three commonly used computer simulation models:

GLEAMS (Groundwater Loading Effects of Agricultural Management Systems; Leonard *et al.*, 1987): The GLEAMS model is a water-capacity field-scale model, which has been developed to evaluate the effects of land management practices on the movement of chemicals associated with runoff and leaching through the soil and unsaturated zone. The water-capacity method involves the transfer of water from one soil layer to the adjacent downward layer in the soil profile once the layer above exceeds its water-holding capacity (i.e., field capacity). The GLEAMS model allows soil and climatic characteristics and land management practices to be varied over time.

LEACHM (Lspching Estimation And Chemistry Model, Hutson and Wagenet, 1995): The LEACHM model simulates general vertical water and solute movement, and LEACHP is the module of the LEACHM model used to simulate pesticide degradation and transport. It is a more complex model than GLEAMS in that it requires more detailed input variables to model water movement using the Richards equation and the convection–dispersion equation (CDE) for solute (pesticide) transport.

HYDRUS-2D (Simunek *et al.*, 1996): The HYDRUS-2D model solves the Richards equation for saturated–unsaturated water flow, uses a

Table 1: Comparison of model requirements for GLEAMS, LEACHM, and HYDRUS-2D

GLEAMS	LEACHM	HYDRUS-2D
Overview		
<ul style="list-style-type: none"> one-dimensional water capacity functional model that uses capacitance to simulate water flow and mass flow and a linear sorption isotherm to simulate solute transport 	<ul style="list-style-type: none"> one-dimensional finite difference mechanistic model that uses the Richards equation to simulate water flow and the convection–dispersion equation and a range of sorption isotherms to simulate solute transport 	<ul style="list-style-type: none"> two-dimensional finite element mechanistic model that uses the Richards equation to simulate water flow and the convection–dispersion equation to simulate solute transport
Soil data		
<ul style="list-style-type: none"> depth of each horizon (maximum of 5) 	<ul style="list-style-type: none"> depth of profile (segments are evenly spaced) 	<ul style="list-style-type: none"> depth of each horizon (variable thickness allowed for each horizon—maximum of 10) number of mass balance zones (maximum of 10)
For each horizon (GLEAMS, HYDRUS-2D) or segment (LEACHM)		
<ul style="list-style-type: none"> clay and silt % porosity, field capacity, wilting point K_{sat} bulk density organic matter content 	<ul style="list-style-type: none"> silt and clay % and particle density organic carbon % water retention curve characteristics (Campbell's a and b) hydraulic conductivity at a defined matric potential bulk density dispersivity (longitudinal) 	<ul style="list-style-type: none"> water retention curve characteristics $\theta_r, \theta_s, \alpha, n^\dagger$ K_{sat}^\ddagger organic carbon % bulk density dispersivity (longitudinal and transverse) diffusion coefficient
Other		
<ul style="list-style-type: none"> SCS curve number (runoff parameter) soil evaporation slope of land 		
Climate data		
<ul style="list-style-type: none"> daily rainfall monthly mean minimum and maximum temperature monthly mean radiation monthly mean wind run monthly mean dew point 	<ul style="list-style-type: none"> daily rainfall weekly evapotranspiration weekly mean temperature weekly mean amplitude of temperature variation 	<ul style="list-style-type: none"> daily rainfall potential evaporation rate potential transpiration rate
Pesticide data		
<ul style="list-style-type: none"> initial pesticide concentrations Solubility K_{oc} § for each pesticide degradation rates for each pesticide 	<ul style="list-style-type: none"> initial pesticide concentrations Solubility saturated vapor density degradation rates for each pesticide (can be temperature and soil moisture dependant) 	<ul style="list-style-type: none"> initial pesticide concentrations K_d ¶ for each pesticide degradation rates for each pesticide

θ_r , residual soil water content; θ_s , saturated soil water content; α parameter α in the soil water retention function; n , parameter n in the soil water retention function.

‡ Saturated hydraulic conductivity.

§ Distribution coefficient for soil organic carbon.

¶ Distribution coefficient

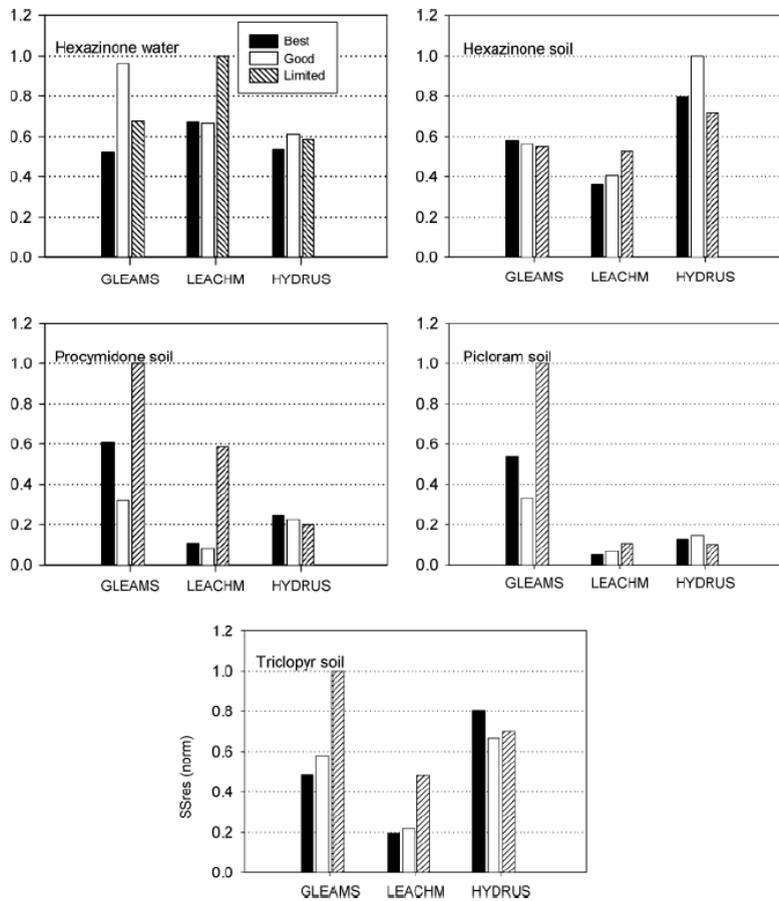


Fig. 2: Comparisons of the range of SS_{res} values (from “best” soil value to “limited” soil quality value) for each of the models run with opti-mized, USDA, and laboratory (for procymidone) pesticide parameters. Boxes show maximum and minimum range with line through box indicating median value. The term SS_{res} is the sum of squares residual, and Hex, Pro, Pic, and Tri are hexazinone, procymidone, picloram, and triclopyr, respectively

convection–dispersion equation for solute transport, and includes provisions for linear and nonlinear equilibrium or non-equilibrium adsorption, and first-order degradation (Simunek *et al.*, 1996). The HYDRUS-2D model was used for simulating pesticide transport through both the unsaturated zone and saturated zone (incorporating observations from monitoring wells downgradient of the plot) at the same experimental site.

The performance of the models was quantitatively evaluated by comparing the simulated pesticide leaching results from the three models to the observed data using three goodness-of-fit (GOF) parameters, namely sum of squares residuals (SS_{res}), coefficient of residual mass (CRM), and coefficient of determination (r^2). Goodness-of-fit parameters provide a suitable mechanism to quantitatively compare the results of simulated models to actual values and to characterize systematic under- or over-

prediction (Loague and Green, 1991). The following GOF statistics were selected for evaluation of the parameter estimates and the leaching models:

$$\text{Residual sum of squares } (SS_{res}) = \sum (S_i - O_i)^2 \dots (23)$$

The residual sum of squares is the sum of the squared deviations of the observed values for sample i (O_i) from the simulated values of sample i (S_i). The SS_{res} value is a commonly used parameter that is unit dependent with a lower limit, which is an ideal value of zero, and no upper limit.

Coefficient of determination (r^2) =

$$\frac{[\sum (O_i - O_m)(S_i - S_m)]^2}{\sum (O_i - O_m)^2 \sum (S_i - S_m)^2} \dots (24)$$

The coefficient of determination used here is the square of the correlation coefficient. The variables

O_m and S_m represent the means of the observed and simulated data, respectively. The upper limit and ideal value for r^2 is 1.

$$\text{Coefficient of residual mass (CRM)} = \frac{\Sigma(O_i - S_i)}{\Sigma O_i} \dots(25)$$

The coefficient of residual mass (CRM) value provides a comparison of the mass of the pesticide observed and simulated within the profile irrespective of its distribution. The CRM value can be positive or negative and gives the ideal value of zero when the observed and the predicted concentrations of the contaminant throughout the profile are equal.

Comparison between models

The three main variables compared were the pesticide sorption and degradation rate/half-life of the pesticide, soil physical property data, and three different leaching models. Analysis of variance of the GOF values for the three models indicated that for all pesticide–sample media combinations and GOF parameters there was no significant difference between the models (at $p < 0.05$) (Table 2). The output for each model was more dependent on the

quality of the pesticide sorption and degradation data. Within the optimized data LEACHM was overall the best-performed model though there was some variation between pesticides (Fig. 1).

Conclusion

Overall, GLEAMS results were generally the least accurate, which is probably a reflection of the less complex handling of water movement and the restriction of five soil layers in the model compared to the eight layers identified at the site (Close *et al.*, 2003a). Rekolainen *et al.* (2000) indicated that GLEAMS is designed to simulate chemical transfer in surface runoff and field edge and in percolation water out of the root zone. As such, GLEAMS may not be the most suitable model for smaller scale plots, such as used in these experiments. One reason for the better performance of LEACHM compared to HYDRUS-2D in this study is that HYDRUS-2D only outputs the liquid phase resident concentrations, and thus direct calibrations can be made only against soil water data. The calibration of soil concentrations was indirectly performed through calibration of soil mass in each subregion of the model domain, which can lead to incorporation

Table 2: Analysis of variance p values for comparison of goodness-of-fit (GOF) values from simulations run with the three different models (GLEAMS, LEACHM, and HYDRUS-2D), the different sorption and degradation parameters, and the different soil quality data.

Pesticide and sample medium	ANOVA factors	P†		
		SS _{res}	CRM	r ²
Hexazinone–water	models	0.92	0.82	0.93
Hexazinone–water	K _{oc} and half-lives	0.00*	0.00*	0.04*
Hexazinone–water	soil group	0.62	0.73	0.02*
Hexazinone–soil	models	0.09	0.07	0.30
Hexazinone–soil	K _{oc} and half-lives	0.00*	0.00*	0.00*
Hexazinone–soil	soil groups	0.85	0.61	0.83
Procymidone–soil	models	0.42	0.74	0.73
Procymidone–soil	K _{oc} and half-lives	0.00*	0.00*	0.00*
Procymidone–soil	soil groups	0.86	0.83	1.00
Picloram–soil	K _{oc} and half-lives	0.00*	0.00*	0.00*
Picloram–soil	soil groups	0.87	0.55	0.87
Triclopyr–soil	models	0.92	0.62	0.98
Triclopyr–soil	K _{oc} and half-lives	0.00*	0.00*	0.00*
Triclopyr–soil	soil groups	0.96	0.80	1.00

*Significant at the 0.05 probability level.

† SS_{res}, sum of squares residual; CRM, coefficient of residual mass; r², coefficient of determination.

of some error if the soil layers are thick. This may be a significant factor in this study as most of the observed data were from soil samples.

Therefore, LEACHM simulated observed data more accurately than GLEAMS regardless of the complexity of the soil data and also more accurately than HYDRUS-2D with higher quality soil property data.

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