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OFFSITE TRANSPORT OF PESTICIDES IN WATER: MATHEMATICAL MODELS OF PESTICIDE LEACHING AND RUNOFF

(Technical Report)

Prepared for publication by

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Pesticides report 35. Offsite transport of pesticides in the aqueous phase: Mathematical models of pesticide leaching and runoff (Technical Report)

Synopsis

The process of modeling the leaching and runoff 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 leachate and runoff 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 and runoff 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, but have not been as widely used. The GLEAMS model is appropriate for quantifying runoff potential in simple, field-scale drainage patterns. The more complex SWRRBWQ model is more appropriate for watershed-scale assessments. The most appropriate use of these computer simulation models is to rank the contamination potential of a particular pesticide at several sites or rank several pesticides at one site. Another excellent application of these models is to calibrate them to fit the results of an intensive field study at one site, and extrapolate to other points in time and space for the same pesticide. One should always recognize the variability in natural processes and field conditions, and use probabilistic (stochastic) analysis whenever possible. More model validation and calibration is needed in tropical climates and in special situations such as turf, forests and orchards.

Contents

LIST OF ACRONYMS/ABBREVIATIONS

AF	Attenuation Factor	HSPF	Hydrological Simulation Program-Fortran (J)
ARM	Agricultural Runoff Model	LEACH	Leaching Evaluation of Agricultural Chemicals
CALF	Calculation Flow	LEACHM	Leaching Estimation And Chemistry Model
CMLS	Chemical Movement in Layered Soils	MUSLE	Modified Universal Soil Loss Equation
CREAMS	Chemicals, Runoff, and Erosion from Agricultural Management Systems	PELMO	Pesticide Leaching Model
EC	European Community	PRZM	Pesticide Root Zone Model
ECPA	European Crop Protection Association	RZWQM	Root Zone Water Quality Model
EPA	Environmental Protection Agency	STREAM	Stream Transport and Agricultural Runoff of Pesticides for Exposure Assessment Methodology
EPIC	Erosion-Productivity Impact Calculator		
GLEAMS	Ground Water Loading Effects of Agricultural Management Systems	SWRRB	Simulation for Water Resources in Rural Basins
GUS	Groundwater Ubiquity Score	VARLEACH	Variable Leaching

1. INTRODUCTION, PURPOSE, AND SCOPE

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 (ref.1). Mathematical models--assemblages of concepts in the forms of mathematical equations that portray understanding of natural phenomena (ref.2) -- can be useful tools to simulate reality when applied properly.

The purpose of this paper is to provide an introduction to the use of mathematical models to simulate pesticide leaching and runoff. Specifically, this paper reviews the more important and/or well-known models in this area, describes how they are used, and provides information that will aid the reader in model selection. The scope of the paper is limited to pesticide loss by water transport from the site of application. Thus pesticide leaching through the root zone and pesticide runoff past the edge of the field are both discussed in detail but transport after the pesticide has entered ground water and surface water are not. This paper does not provide detailed instructions for use of the models but does cite references that contain such guidance.

The models described herein have been designed for three different purposes: screening, regulation/exposure assessment, and research. Screening models usually have the least demanding input data requirements and are best used in an advisory mode for setting priorities and identifying potential problems. Regulatory models can have extensive input data requirements and are frequently applied in quantitative assessments of potential chemical impacts. Research models are usually the least user-friendly, have extensive data requirements, and have varying types of applications.

Models represent complex processes but can be either simple or complex in their construction and execution. Accordingly, we present below categories of models generally in order of increasing sophistication and complexity. This follows a tiered assessment strategy that is often appropriate, particularly in a regulatory environment; i.e., one would tend to use a simple screening or indexing model prior to applying the more complex models. But the reader is cautioned to use conservative assumptions in the first tier of assessment, to reduce the chance of missing a potential problem (a false negative). This is necessary due to the high degree of uncertainty associated with these first-tier models. Thus a model user would not have confidence that the screening model results quantify reality precisely, but, given an appropriate set of conservative assumptions, the user could feel confident that the true answer at least lies below some concentration of concern.

The target audience is anyone who wishes an introduction to environmental simulation modeling--the kinds of models available, their credibility, and their use in regulation and research. Because models serve as a concise and precise summary of knowledge of the behavior of pesticides in the environment, exploring them is an extremely efficient way to access this knowledge.

2. THE MODELED SYSTEM: PESTICIDE TRANSPORT BY RUNOFF AND LEACHING

Scope. This discussion focuses on pesticide transport by mass flow of water and ignores vapor transport and molecular diffusion. The discussion is also restricted to pesticide losses from the surface or below the upper meter or so of the soil profile. Given this emphasis, the runoff and leaching of pesticides may be described in terms of the hydrology and soil erosion of agricultural fields.

2.1 Hydrology

All models start by characterizing the mass of moisture within the soil body and the processes that move it vertically or horizontally. The three forces that are responsible for mass flow are gravity, hydraulic head, and

surface tension. These forces act at all times to attempt to establish hydrologic equilibria, but equilibria are almost never approached because of constant additions or subtractions of moisture from the system by evaporation, plant uptake and transpiration, precipitation, and runoff. (Run-on is also possible but not usually considered).

Soil characteristics, crop or plant growth, and weather each strongly affect the rates and amounts of water flow, and each affect it in strongly different ways. Soil characteristics vary spatially, especially in the vertical dimension. Crop top and root growth and moisture extraction are so complicated spatially that only simplistic representations have been undertaken. Fortunately, the effects of crop growth and root uptake on soil moisture are well defined empirically for crops for agronomic reasons, and tend to be overwhelmed by precipitation events.

Weather is stochastic and must be input either as a probability distribution function or as a time series from real or generated data (ref.3). In some cases it is possible to simplify things by assuming a constant moisture input, i.e., a steady flow of percolating water occurs (e.g.,(ref.3,4,5,6)). Generally, however, real weather data are used for the site in question.

Hydrologic processes. When rain, irrigation water, or melting snow contact the surface of a soil, water is absorbed by capillary attraction and travels downward as a "wetting front" through the smaller pores of the soil. This capillary action is bypassed once the soil becomes saturated. The movement of water from the surface to the body of the soil is called infiltration. As the soil grows wetter its smaller pores fill up, its capillary attraction for water decreases and its rate of infiltration decreases. If the infiltration rate becomes less than the rainfall rate the soil becomes saturated at the surface, flow downward begins to occur through all sizes of pores and is called saturated flow, and runoff begins. (The term "runoff" usually implies overland water flow, but in many cases entrained sediment is included in the term.) This interaction between precipitation and infiltration rates is the critical process determining whether runoff will occur. Downward water flow within the soil is sometimes called percolation and also, wrongly, leaching; the latter term will be used only for the movement of solutes in the water, e.g., pesticides leach downward, transported by percolating soil water.

If percolating water reaches an impeding (low-conductivity) soil layer it may flow along the top of that layer and re-emerge as part of runoff; such a flow path is called interflow and can lower or raise concentrations of solutes in runoff water (ref.7).

Infiltration, percolation and runoff are complicated by many variables. Soil variables include initial moisture levels, micro- and macroporosity, moisture holding capacity, clay lattice type (expanding or non-expanding), surface chemistry, wetting capability, hydraulic conductivity, organic matter content, and the variation of all with depth. Field variables include topography, geometry, crop cover, crop residue cover, surface roughness, soil surface albedo, tillage, drainage. Meteorological variables include initial heat content of soil, air and soil temperatures, sunlight, precipitation timing and intensity (even during events), and wind. Many of these variables interact. The only way to construct this huge multidimensional variable space is to attempt to define all the interactions and increment the descriptions through time steps small enough to account for each variable's temporal changes. The basic purpose of integrating these variables is to calculate the water balance and, ultimately, pesticide transport.

2.2 Erosion

Second in importance to water flow, but important in resource conservation concerns, is soil erosion (ref.8). In many areas sediment is the most important nonpoint pollutant generated by agriculture (ref.9). Even under the best management, small amounts of erosion can occur. It is not only an important pollutant of water resources but represents a loss of topsoil resources as well (ref.10). For our purposes, sediment is also important because it can be the vehicle for transport of nutrients and pesticides that are highly water-insoluble or strongly bound to eroding soil. Such pollutants may be too insoluble or soil-bound to be transported in runoff water or percolation water, but erosion can mobilize them into runoff.

Erosion and its control is a well-developed, very pragmatic science. Once one has defined the hydrology of a field, erosion may be rather well predicted, again assuming one has soil erodibility information about the site

of concern. This capability is the result of the fact that erosion prediction is the result of an enormous amount of empirical research.

Erosion is divided into two (overlapping) processes (ref.11). Laflen erosion is the detachment of soil by water flowing in defined streams (which may be very small rills in the field) and is a result of hydraulic shear forces. Interrill erosion is the detachment of soil by raindrop impact occurring in the presence of shallow flows before the flows are concentrated into rills. The dominant variable controlling interrill erosion is rainfall energy which depends on the size distribution and numbers of drops impacting the soil.

Both types of erosion are sensitive to slope, soil properties such as shear resistance and texture, slope concavity, crop residues, crop foliage cover, and erosion control management practices such as contour plowing and conservation tillage.

Erosion and pesticide runoff. It is important to recognize that only a fraction of pesticides in use today are so strongly soil-bound as to be transported principally in the sediment phase of runoff. Soil conservationists often state that erosion control will result in chemical pollution control as well. This is true only for extremely soil-bound pesticides such as paraquat, pyrethroid insecticides and other nonionic, hydrophobic species (ref.12).

2.3 Pesticide transport runoff

Once percolation and water runoff are well-characterized, pesticide leaching and runoff can be fairly well predicted, for some cases, using rather simplistic models for soil extraction by percolation and reemergence of runoff water (ref.13). All current models predict runoff of pesticides by assuming an attempted equilibration (not necessarily complete) between runoff water and the topmost thin layer at the soil surface. Water is assumed to penetrate this layer due to the hydrostatic pressure of raindrop impact (ref.14), reemerge as other drops apply pressure nearby, and join overland flow. This concept has never been experimentally verified, though Leonard (ref.15) has shown that pesticide runoff concentrations are proportional to soil concentrations in the top cm of soil. The mechanism has been incorporated in various versions in all the pesticide runoff models, notably CREAMS/GLEAMS and ARM/HSPF. (CREAMS, GLEAMS, and HSPF are complex runoff models that are described in section III(D).)

Since infiltration and percolation usually precede runoff during an event, the leachability of a pesticide can determine how much remains near the surface and available for runoff (ref.15,16). Similarly, rainfall can lower the amounts of pesticide in later runoff events (ref.17). Thus we have two conflicting water-quality-impacting processes. Pesticides that are highly mobile are more likely to leach to ground water, but unlikely to occur in runoff; those pesticides that are extremely soil-adsorbed are more likely to be available for runoff, but will not leach to ground water through normal capillary flow. Thus current efforts to re-formulate pesticides to inhibit their leaching (ref.18) may only make them more available for runoff.

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. Solutions to this equation are available for steady water flow (ref.19)but for realistic, weather-driven applications numerical schemes are required. Flow through a homogeneous porous medium is complex enough; spatial variability in flow rates can become large even in a small volume of soil due to variations in pore size and surfaces. Macropore flow can overwhelm all other processes when flow is near saturation e.g., (ref.20). (Examples of macropores are worm holes, decayed root channels, and other open pathways in highly structured soils.) Spatial variability simply adds another dimension to an already formidable problem. (See the discussion of "The Uncertainties in the System" below). Thus we are aware of great complexity in solute transport in soils; but all current models except the most extreme "research" models (ref.19) describing processes in one dimension are simplistic representations of reality.

"Management" models (ref.19)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

$$K_d = C_s/C_w \quad (1)$$

where C_s (in milligrams/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 nonequilibrium 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 $K_d = C_s^{1/n}/C_w$ (ref.21).

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:

$$K_{oc} = K_d/F_{oc} \tag{2}$$

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.

2.4 Pesticide properties

The above discussion makes it clear that several fundamental properties of pesticides provide important and basic information on their potential for runoff and leaching. Efforts to develop consensus values for these data are underway in the US (ref.22).

2.4.1 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

$$\log K_{oc} = - 0.55 \log Sol_w + 3.64 \tag{3}$$

where Sol_w is the water solubility in mg/L (ref.23). Similarly, (ref.22) Wauchope, et al. (1992) has found the following relationship to hold true for a wide variety of pesticides:

$$K_{oc} = 3000/\sqrt{Sol_w}. \tag{4}$$

But these relationships only hold for nonionic pesticides.

2.4.2 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. Clearly the probability of either loss is proportional to the amount of pesticide present, whether on foliage or on or inside the soil.

Environmental degradation is the result of a variety of processes (photodecomposition, 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:

$$C_{t_2} = C_{t1} \; exp[-k(t_2 - t_1)] \tag{5}$$

where C_{t_2} is the concentration at time 2 and C_{t1} 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

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

Simple ("first-order") exponential decay is often too simple a model, particularly for microbial processes. Many studies have shown that the most exposed residues in a pesticide application degrade first, leaving protected residues to degrade more slowly. Thus, the apparent half-life appears to increase in time (ref.24,25,26). But the simple model is adequate for most cases because it is the earliest events which are the most important, in terms of amount of loss.

Persistence may be the single most important pesticide property to determine the potential environmental impact of a pesticide for runoff (ref.16). Similarly, the soil half life was found to be higher for pesticides that were detected in ground water in the U.S. EPA's National Pesticide Survey than those that were not, at the p=0.02 level of significance (ref.27).

2.5 Pesticide application methods and formulation types

2.5.1 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 runoff/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 (ref.28). Incorporation of soil-applied pesticides most likely increases persistence for the same reason. Indeed, if incorporation could be done in such a manner that little or no pesticide were left at the soil surface (such is seldom the case unless injection is included under the definition of incorporation) it is probable that runoff losses could be nearly completely eliminated. Consider that a pesticide is spread out in a very thin layer on application; even low volatile chemicals will experience volatility losses under such conditions.

No current pesticide transport model adequately models the physical processes involved in transporting pesticides from foliar deposits to runoff. In general the models simply add a "washoff fraction" of foliar-deposited pesticides to the water at the surface but it is clear that is a vast simplification.

2.5.2 Formulation. Several reviews (ref.16,24,15,12) 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. No current pesticide transport model deals with the differences in dissolution kinetics and transportability of different formulation types.

2.6 The uncertainties in the system

Any attempts to model an environmental system has uncertainties. It is important for the modeler to be aware of the uncertainties. Whenever feasible, uncertainties should be quantified and the results presented in terms of probability distributions or confidence intervals. The different types of uncertainties are described below.

2.6.1 Model uncertainty. 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 (as of 1994). Another example could be the incorporation of algorithms that do not represent reality properly, e.g. a leaching model that only allows for a single transformation rate constant throughout the soil profile.

Good model validation studies can help allay concerns about model uncertainty. Acquiring thorough understanding of the algorithms prior to application of the models can help as well.

2.6.2 Parameter uncertainty

2.6.2.1 Pesticide parameters. The most critical pesticide chemistry parameter for leaching assessment is the degradation rate constant(s). 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_20, 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. The reason why this uncertainty consideration is mandatory is that it is known to be highly variable. For example, the coefficient of variation (CV) for top soil metabolism or dissipation of 31 pesticides was usually greater than 40%, and averaged 73% (ref.29). The soil half life for carbofuran can vary one order of magnitude (ref.30). These are examples of half-life variations by geographic location and soil type.

Smith, et al. (ref.31) reported CVs for pesticide transformation that ranged from 7 to 202% and averaged 62 ± 44%, and were generally less than 100 (excluding organochlorines). The CVs for pesticide concentration results from two field studies was 40 to 450%. The CVs generally increased over time.

It is also important to note that k varies with depth as well, usually decreasing significantly with increasing depth. Unfortunately there are limited data to demonstrate this. Kördel et al. (ref.32) found decreases in degradation rates that ranged between approximately 3 and 18 fold when comparing deeper with shallower soil profiles. They studied simazine degradation for 150 days (ref.33). Donigian and Carsel (1987) estimated that k in the root zone was reduced by 50% below the root zone during a series of PRZM simulations, based on data from aldicarb and atrazine. 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 (ref.34).

There appears to be less variability in K_{oc} which is expected since it is supposedly a constant. Rao and Davidson (ref.29) critically reviewed the literature and obtained CVs for K_{oc} values of 42 pesticides. The average of those values was 62%.

The STREAM and LEACH manuals described below provide excellent examples of the sensitivity of sophisticated runoff and leaching models to changes in k and K_{oc}. Loague, et al. (ref.35) demonstrated that uncertainties in K_{oc} and k can introduce significant uncertainties in the Attenuation Factor model (section III(B)).

Pesticide formulation types and application sites, e.g. foliar vs. soil, may be more important parameters for determining runoff potential than k or K_{oc} when pesticides are applied close to rainfall events (ref.36).

2.6.2.2 Field parameters. There are great uncertainties in field parameters. This is why modeling assessments for specific sites are more reliable compared with assessments using field parameters from the literature, especially when the site is sampled/characterized.

Some field parameters vary little for a particular field. Unfortunately, significant parameters have variability. For example, Jury (ref.37) evaluated the spatial variability of several soil properties relevant to pesticide leaching potential. He found little variability for bulk density (ρ) for particular sites -- average coefficient of variation (CV) = 10 %. Thus only six samples from a particular field would yield a 95 % probability of determining a 20 % variation in ρ if it exists. On the other hand, the average CV of the saturated hydraulic conductivity calculated from the data in Jury (ref.37) is 119%, indicating that 42 samples would be required from a site to detect a 100% variation in K -- 502 samples would be required to detect a 20% variation! The average variation in K_{sat} of all materials presented by Dean, et al. (ref.38) was 200%.

Loague et al. (ref.35) found minimal variability in ρ in five soil orders common to Hawaii and many other areas of the United States. 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 had an even lower CV.

The U.S. EPA's PRZM2 leaching model (discussed in Section 3.4.1) has a sophisticated uncertainty analysis package using the Monte Carlo method. One of the sensitive hydraulic parameters EPA recommends varying in the Monte Carlo analysis is the van Genuchten alpha parameter, (R. Carsel, U.S.EPA, Personal Communication 1994), an empirical parameter that is used to solve the Richards equation of water flow (section 3.4.1).

The CV of alpha can vary from 20% to 160%, depending on the soil type (section 3.4.1).

2.6.2.3 An integrated pesticide parameter and field parameter uncertainty analysis. Discussions above and in sections 3.4.1 and 4.1 refer to the sophisticated probabilistic module called Monte Carlo analysis, which provides a rigorous way to estimate the ranges of possible leaching and runoff outcomes. But this technique is not always available to modelers. Therefore the following alternative approaches are recommended when Monte Carlo analysis is not available.

For runoff modeling, choose one or more intense rainfall events of a known recurrence frequency, e.g., a 2 yr-return, 24 hr. storm event. 'Apply' the pesticide shortly before the event, say, 2 days prior. Compute the probability of the two events co-occurring, and present that probability along with the results.

For leaching modeling, one can assume the worst case obtains when certain parameters all vary simultaneously in favor of leaching. Then subtract the best estimate of pesticide leachate mass from the worst case mass to obtain a value that approximates four to six standard deviations (R. Parrish, Athens, Georgia, personal communications, 1991). Divide that range by four to approximate the standard deviation in each pesticide leachate calculation. Then add two standard deviations to the best estimate (or mean) case to approximate the upper 95% confidence interval.

The first author developed this procedure to be used with PRZM2 before the Monte Carlo module became fully operational. The worst case was estimated by running the model after subtracting one standard deviation from the dissipation rate constants in each layer, adding one standard deviation to the hydraulic conductivity, and subtracting one standard deviation from the K_{oc}. The assumption is that it would be unlikely that all three parameters would vary simultaneously in the direction favoring leaching.

In a theoretical study, Fontaine et al. (ref.39) found the PRZM parameters whose variability had the greatest influence on leaching depth (not concentration) were rainfall, runoff curve number, half life, Koc, and five other parameters.

3. THE MODELS

This section provides advice on selecting models, and it summarizes information on the most frequently used models, including models with a very wide range of sophistication and input data requirements.

3.1 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.

Following are some criteria that should be used when selecting a simulation model.

3.1.1 Validation and calibration with experimental data. All computer models have to be validated by means of experiments and, if necessary, have to be calibrated for specific environmental situations. At present a

number of computer models are available to predict the leaching behavior of pesticides into ground water. Substance-specific sorption data and degradation data are needed, which are generally obtained by laboratory experiments. When simulating a chemical's outdoor behavior with a simulation model based on laboratory data, a calibration of the results may be necessary. Otherwise, significant deviations between predicted results and reality may result, unless site-specific sorption and $t½$ data are used.

3.1.2 Appropriateness of model for task at hand. Due to the complexity of transformation and transportation processes all models suitable for estimating the fate of chemicals in the environment are based on simplifying assumptions and are thus restricted to a range of specific problems. Simulation models can only be applied successfully if the models are properly chosen for the problem to be solved.

Example: To make a first rough estimation of the behavior of chemicals in the environment a calculation using the method of Mackay (ref.40) (Level 1) which calculates the distribution of chemicals between different phases but neglects degradation processes, is suitable. Estimations on this basis show in which parts of the environment (water, soil, air) chemical stress may be expected without providing a quantitative assessment of amount and time. If this information, which is calculable in a second, is sufficient for a needed decision, it is not necessary to use more complicated models which require more input data and more time. On the other hand more precise estimates require more complex models.

3.1.3 Model availability and user support. One should consider the amount of technical support available to the user after the model is acquired. Is the model easily obtained? Will updates be mailed automatically? Is the technical support group available during normal working hours, considering differences in time zones?

3.1.4 Availability of input data. Computer models have to be designed in a way that the required input parameters (in general a combination of data for a specific scenario and data of a specific chemical) can be made available with justifiable effort. The application of simulation models is not justified when the needed input data can only be obtained with undue effort as compared to the results obtained.

On the other hand models which are designed considering only actually available data delay progress in the understanding of important environmental processes. Therefore a permanent dialogue between scientists developing models and experimental scientists is required which considers both the state of the art and future requirements, in order to guarantee the improvement of the models as the data available shows.

The PELMO (leaching) and EXAMS (surface water) models come equipped with some "canned" environmental scenarios. A U.S. EPA modeling package called PATRIOT contains environmental data intended for use with the PRZM model. All of these models are discussed below.

3.1.5 User friendliness. Models must be user-friendly. In most cases scientists involved in developing programs and users of models are not the same persons. Programmers, who are in general scientists with good capabilities in data processing, often spend much effort and time programming mathematic algorithms, and neglecting the considerations of the potential users of the programs. Therefore many programs consist of too many input parameters not differentiating between parameters which are important and those which hardly influence the result. During complicated and time consuming calculations the user should be informed on the state of the simulation process at any time to be able to evaluate the duration of the simulation process. A user-friendly model should further contain a graphic program comprehensively representing the most important results of the simulation instead of unclear lists and tables.

Unfortunately many environmental simulation programs are not user-friendly, but this is improving. At present, application of many potentially useful models is hampered when potential users are not able to apply the model with justifiable effort.

3.2 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 precalculated nomograms (graphs). They are at best semi-quantitative and most useful for predicting very safe or very risky situations.

3.2.1 Screening criteria

3.2.1.1 EPA criteria. A review of data on the presence of pesticides in ground water from monitoring studies in the USA by Cohen et al. (ref.30) identified twelve pesticides that had regularly occurred in such supplies as a result of normal agriculture use. From these studies, as well as computations performed by the first author (S. Cohen, personal communication, 1992) a number of key environmental parameters and field conditions were identified that could aid in predicting which compounds will leach to ground water.

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-m^3/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.

According to the authors,"... it appears that when all the following chemical characteristics and field conditions appear in combinations, the potential for ground water contamination is high." No prioritization of these criteria was provided though some will be more influential than others. This was one of the first attempts to identify pesticides having the potential to leach to ground water without using a computer. Although the criteria have generally been found to be successful, most of the newer methods presented below are more sophisticated and dynamic.

3.2.1.2 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 (ref.41). The first tier is based on to the EPA/Cohen, et al. (ref.30) criteria described above.

3.2.1.2.1 Mobility.
- Water solubility > 30 mg/l
- Organic carbon sorption constant (K_{OC}) < 500 ml/gm
- Sorption coefficient (K_D) < 10 ml/gm

3.2.1.2.2 Degradability in soil.
- DT_{50} > 21 days

3.2.2 Indexing models

3.2.2.1 GUS. The GUS index (or Ground Water Ubiquity Score) (ref.42) 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 ($t_{½}$) and the partition coefficient between soil organic carbon and water (K_{oc}). The index is calculated using the empirical equation.

$$GUS = \log (t_{½} \text{ soil}) \times (4.0 - (\log K_{oc})) \quad (7)$$

Scores assigned with this screening index show good agreement with results from ground water monitoring surveys. 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. Volatility is not required since the screening methodology is already based on measured field half-lives, which account for volatilization. (This can become a problem when using more sophisticated computer simulation models that have explicit considerations for volatilization.) 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

The important values of 1.8 and 2.8 bracket the region in which transition occurs from leachers to non-leachers. In practice these regions could be used in the following way. Compounds that fall in the leacher or transition range (1.8-2.8) would require further investigation by the more sophisticated modelling programmes. Compounds which fall in the non-leaching region could safely be exempted from further consideration as possible leachers.

3.2.2.2 Jury. Jury et al. (ref.5) developed a simplified pesticide transfer model for determining potential pesticide leaching into ground water, using idealized, but physically-based transport processes, and including biodegradation. The model assumes steady water flow, equilibrium linear adsorption and depth-dependent first order biodegradation, and predicts travel times to ground water and residual concentrations, depending on soil and environmental conditions. Representative values for soil properties, depth to ground water and drainage rates are combined to produce different scenarios that represent low and high potential for pesticide migration to ground water. The model is reduced to a simple linear inequality between the partition coefficient between soil organic carbon and water (K_{oc}) and the biochemical half-life ($t_{½}$). Therefore the model enables the classification of leaching potential based upon K_{oc} and soil half life.

The model was applied to 50 pesticides for which the physical data were known. The plot of K_{oc} vs $t_{½}$ included two lines representing the boundaries for the low and high pollution potential scenarios. Those compounds that did not satisfy the inequality test appeared on the "high risk" region whereas the compounds that satisfy the inequality appeared in the "low risk" region.

As with the other screening procedures, this procedure is only qualitative and relies on a number of assumptions that may not be met under natural conditions. Both K_{oc} and $t_{½}$ for a single compound may vary considerably and result in the compound moving from one region to another. The model is useful in classifying ground water pollution potential and possibly in interpretation of observations of ground water contaminants. If a chemical, predicted to be of low risk and is located in ground water, then it could indicate the $K_{oc}/t_{½}$ values are incorrect, or that the mode of entry is not typical of normal agricultural practice, i.e., point source contamination.

The Jury model and the other models described in this section may have potential in the early estimation of possible environmental problems with candidate agrochemicals. Early recognition of such problems can be combined with efficacy and profitability projections in assessing the development potential. A prototype screening tool based upon the Jury solution has been developed in which a high level of user friendliness has been achieved. The interface has the "look and feel" of an analytical instrument in which adjustments via dials to inputs results in prompt changes to a 3D concentration surface and log/linear graphs of soil water concentration (McFarlane (SRC) personal).

3.2.2.3 Attenuation Factor. Rao, et al. (ref.43) 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

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

where

M_2 = mass lost below the root zone,
M_0 = amount of pesticide applied to the soil surface,
B = k(tr),
k = degradation rate constant, and
tr = pesticide travel time in the vadose zone.

The travel time tr is calculated by the following equation:

$$tr = (L)(RF)(FC)/q, \quad (9)$$

where

L = the depth for calculation,
RF = retardation factor ($1 + \rho K_d/\theta$),
FC = field capacity, and
q = net recharge rate.
[RF can include a volatilization term as well.]

Rao et al. (ref.43) evaluated their ranking scheme relative to others and applied it to 41 pesticides. They determined that several nematicides and herbicides -- EDB, DBCP, aldicarb, carbofuran, bromacil, terbacil, simazine, and cyanazine -- were ranked as having a high potential to leach to ground water in Florida, USA. Kleveno et al. (ref.44) indicated that AF predictions of mass loss reasonably approximate those of the more complex Pesticide Root Zone Model (see below, Section 3.4.1).

AF is available as an option in the CHEMRANK screening model, which is used to rank the relative leaching potential of a suite of chemicals (ref.45).

3.2.2.4 SCS soils/pesticides screening procedure. The USDA Soil Conservation Service (SCS) screening procedure developed by Goss (ref.46,47), determines leaching and runoff indices for pesticides and combines them with leaching and runoff indices for soils. The two indices are then used together to determine specific runoff/leaching potential for the combination. For example, a soil with a very low leaching potential is considered safe from leaching for any pesticide, but may be a runoff pollution concern for many pesticides.

The leaching potential for pesticides is identical to the GUS index above. Pesticide runoff indices were determined by a series of runs of the GLEAMS model (see below) for a wide range of pesticide active ingredient properties, under extreme weather conditions. The weather conditions are so extreme that the majority of pesticides are given either a "medium" or "large" runoff potential, which is not correct absolutely. Nevertheless, the results are useful for first-tier comparisons of pesticide runoff potentials.

Runoff potentials are calculated separately for sediment transport and water-phase transport. Based on the GLEAMS calibrations, classes of pesticides could be distinguished. For example, Goss' rules for runoff potential for pesticides are summarized as follows:

High Sediment-Transport Runoff Potential:
Half-life ≥ 40d and K_{oc} ≥ 1000 or
Half-life ≥ 40d and K_{oc} ≥ 500 and Solubility ≤ 0.5ppm

Low Sediment-Transport Runoff Potential:
Half-life ≤ 1d or
Half-life ≤ 2d and K_{oc} ≤ 500 or
Half-life ≤ 4d and K_{oc} ≤ 900 and Solubility ≥ 0.5ppm or
Half-life ≤ 40d and K_{oc} ≤ 500 and Solubility ≥ 0.5ppm or
Half-life ≤ 40d and K_{oc} ≤ 900 and Solubility ≥ 2ppm

High Water-Phase-Transport Runoff Potential:
Half-life > 35d and K_{oc} < 1000000 and Solubility ≥ 1ppm or
K_{oc} ≤ 700 and 10 ≤ Solubility ≤ 100

Low Water-Phase-Transport Runoff Potential:
K_{oc} ≥ 1000000 or
Half-life ≤ 1d and K_{oc} ≥ 1000 or
Half-life < 35d and Solubility < 0.5ppm

All other cases are medium potential.

Goss' criteria have been determined for each of the active ingredients in the SCS/ARS/CES Pesticide Properties Database (ref.22). Thus, a knowledge of the properties of a soil can be combined with those values to screen out pesticides with high pollution potential. SCS soils data for US states has been combined with the Goss pesticide indices using a computer program called NPURG Jenkins, personal communication, 1991. Oregon State University, but that model is no longer being supported and will soon be replaced.

Development of indexing/screening procedures is currently a very active area, and other groups are developing similar approaches (ref.48,49,50,51).

Hornsby (ref.49) has developed a similar soil-pesticide interaction screening model, designed for use by farmers, to help choose which pesticides to use for specific crop/pest combinations. The procedure is referred to as the "kitchen table" procedure, because one can make a decision at home based on filling out work sheets with a pencil--no computation is required. Indices for runoff and leaching are based on the same pesticide properties database as the SCS method, but the method also provides up-to-data information on the Florida Extension Service's recommended pesticides for each crop. Hornsby goes a step further and includes the toxicity of pesticides to humans and aquatic species in the calculation of their runoff and leaching indices.

3.2.3 The STREAM nomograms for runoff screening. The Stream Transport and Agricultural Run-off of Pesticides for Exposure Assessment Methodology (called STREAM) is a technique, designed by the US EPA, for simply and rapidly estimating pesticide concentrations in field run-off water and in associated water bodies (ref.52). It allows an estimation of the mean, maximum frequency and duration of pesticide concentrations and the maximum daily pesticide run-off and its frequency for various agricultural crops and regions across the USA. The procedure is restricted to organic hydrophobic compounds.

STREAM used the Hydrological Simulation Program-FORTRAN (HSPF) (ref.53) model to generate cumulative frequency distributions (nomograms) of pesticide concentrations and loadings in each region. The STREAM user is required to input only the crops (corn, soy beans, cotton, wheat or sorghum) and regions (South East Mississippi Delta, Eastern or Western corn belt) of interest, the pesticide application rate, the organic carbon partition coefficient (K_{oc}), the soil/sediment decay rate constant (k_s) and the solution decay rate constant (k_w). The cumulative probability of runoff is read off a series of nomograms, each of which represents many iterative runs of HSPF using the particular "canned" scenario.

The information can be used by regulatory bodies and agrochemical companies involved a) in registration of new pesticides b) where new ones are proposed for existing pesticides or c) when existing pesticides are being re-evaluated because of concern for human health or environmental risks. Order of magnitude accuracy is generally accepted for these screening level assessments via STREAM for which concentration estimates are required. The model, although more sophisticated than other screening procedures mentioned above, is limited in that it only applies to specific US pesticides/weather/crops scenarios. It is important to know that the scenarios are typical case rather than reasonable worst case or worst case. This is an important consideration for screening level assessments.

EPA has computerized the nomograms. They are available from EPA's Athens, Georgia Research Lab (Center for Exposure Assessment Modelling).

3.2.4 The LEACH nomograms for screening leaching potential. The U.S. EPA has also produced a series of nomograms that describe pesticide leaching potential, analogous to the STREAM methodology for runoff described above. The "Leaching Evaluation of Agricultural Chemicals (LEACH) Handbook" (ref.54) evaluates pesticide leaching potential in corn, soybean, wheat, and cotton-growing areas as a function of soil dissipation rate constants and retardation factors. The latter is a function of bulk density, porosity, and soil sorption coefficients.

The nomograms take the form of exceedance curves, which are very useful for comparing relative leaching potential. For example, according to Figure A7-11 in ref.54, 10% of an applied pesticide would leach 70% of the time if $k = 0.001$ day^{-1}, $R = 5$, and the runoff curve number = 85.

3.3 A computer model with intermediate data requirements

3.3.1 CMLS. CMLS (Chemical Movement in Layered Soils) is a simple "chromatographic" model for the leaching and persistence of nonionic pesticides in soils (ref.4). Up to 25 soil layers of different thicknesses and properties can be input, with each layer being homogeneous within itself. Within each layer pesticide movement occurs only by transport in solution, and equilibration of the pesticide between solid phase and solution phase (adsorption-desorption) is assumed to involve soil organic matter only and K_{oc} values are used (ref.4).

Water balance is calculated in daily time steps based on "effective rainfall" (i.e., infiltration) and evapotranspiration demand. Evapotranspiration removes water from each layer within a defined "root zone" in proportion to the amount of water available. When precipitation occurs the water is distributed from the top layer downward in a "tipping bucket" manner, each layer filling from its initial moisture level to field capacity, and moisture above that amount is passed downward to the next layer.

CMLS provides graphical output that is easy to understand and is an excellent demonstration/teaching tool. It allows quick comparisons of the effects of soil and pesticide properties on mobility. (ref.48,49) have used it to develop guidelines for pesticide selection to protect ground water in Florida.

Data Required
Rooting depth of crop

For each pesticide:
- Soil organic carbon sorption constant K_{oc}
- Persistence time (half-life) in soil
- Time of application
- Depth of application

For each soil layer:
- Depth to bottom of layer
- Organic carbon fraction F_{oc}
- Moisture content at -0.1 bar, -15 bar, saturation
- Bulk density

For Each day of the period simulated:
- Effective rainfall (i. e., infiltration)
- Evapotranspiration demand

Equipment Required
IBM-PC, XT, AT, or compatible with 512K memory and color graphics adapter such as EGA or VGA.

Support
CMLS is published by the Institute of Food and Agricultural Sciences of the University of Florida and sold on an "as is" basis. No formal user support is available.

Friendliness
The manual is well-written and the program is easy to use. The user can generate ASCII input data files which are in a quite simple format, and the program converts them to the needed binary form. Alternatively the user can edit the default data included with the program, which includes pesticide property data for about 40 pesticides and Florida soils. Some familiarity with soil and pesticide terminology is assumed.

Validation Level
CMLS has been compared with field data for transport of bromide and aldicarb in the unsaturated zone in a study by Pennell et al. (ref.55), and its capabilities compared with four other simulation models--GLEAMS, PRZM, LEACHMP and MOUSE. For this data set, CMLS did as well as the more complex PRZM and LEACHMP, and better than GLEAMS and MOUSE, in predicting depth of leaching. All of the models did poorly in describing pesticide concentration distributions with depth, an output that CMLS does not have. These authors argue that for many purposes such as management decision-making and teaching, CMLS, which is the easiest of the five models to use, is the model of choice.

Model Output
Graphical display of (a) rainfall input, (b) % of original application remaining in soil, (c) location (depth) of concentration maxima for pesticides, all as a function of time.

Source
Institute of Food and Agricultural Sciences
Florida Cooperative Extension Service
Department of Soil Science
University of Florida
Gainesville FL 32611-0151
USA

3.4 Computer models with intensive data requirements

3.4.1 Pesticide Root Zone Model (PRZM). The Pesticide Root Zone Model is a dynamic, compartmental model for use in simulating chemical movement in the unsaturated soil systems within and below the plant root zone. The original version was released in 1984 (ref.56a,b). PRZM allows the user to perform dynamic simulations of pesticides applied to the soil or to plant foliage. Dynamic simulations allow the consideration of pulse loads, the prediction of peak events, and the estimation of time-varying mass emission of concentration profiles. This approach overcomes the limitations of the more commonly used steady-state models.

PRZM has two major components: hydrology and chemical transport. The hydrology component for calculating runoff and erosion is based on the USDA Soil Conservation Service curve number technique and the modified universal soil loss equation. Evapotranspiration is estimated from pan evaporation data or by an empirical formula if pan data are unavailable. Evapotranspiration is divided among evaporation from crop interception, evaporation from soil, and transpiration from the crop. The soil profile is segmented into zones or layers based on the horizons of the soil profile.

The two options for calculation of downward water movement are as follows. The first option uses the concepts of field capacity and wilting point where water in excess of field capacity is drained to the next zone. Plant extraction cannot occur once wilting point has been reached, all drainage occurs within a day and no lateral movement is included. These assumptions are best suited for highly permeable soils, such as sands. The second is used for soils for which the assumption of free rapid drainage is not appropriate. Downward water movement can be impeded by a relatively impermeable layer and drainage is no longer forced to occur within the one-day time step. A maximum soil moisture storage capacity is sued for water retardation conditions and

a drainage rate parameter is used to adjust drainage rate. This system only functions when the permeability of the soil layers controls water flow not when water deficits above the water table are controlling. The second hydraulic option is similar to the first, but accounts for restricting layers in the soil profile. To produce soil water and solid phase concentrations, the chemical transport component calculates pesticide uptake by plants, surface runoff, erosion, decay, vertical movement, foliar loss, dispersion, and retardation. A modified version of the convective dispersion equation is coupled with water balance equations to estimate solute movement. A finite difference numerical solution using a backward difference implicit scheme, is employed. The new version of PRZM, PRZM2, uses method of characteristics algorithm to eliminate numerical dispersion (ref.57).

A variety of agronomic parameters can also be varied in PRZM runs. Input data required for this model are generally available. The model can be used with or without calibration and has been successfully tested for both cases (ref.58). The model is supported by the Environmental Protection Agency and is based on intensive research. The model is useful for testing management practices relative to pesticide contamination of ground and surface water quality. However, since PRZM was developed as a leaching model and not a runoff model, it is not sensitive to the effect of surface layer variations on runoff, erosion and runoff-influenced processes, although it does calculate runoff loss of water and solute. The model does not estimate nutrient movement to surface or ground water.

Predictions are made on a daily basis. Output can be summarized for a daily, monthly or annual period. Daily time series values of various fluxes or storages can be written to sequential files during program execution for subsequent analysis. PRZM was designed to run on a DEC PDP 1170 mini-computer using batch jobstream submission, but has been modified to run on personal computers. The code is a compiled version of FORTRAN.

There were significant limitations in the original (Release 1) version of PRZM. A few were obvious to the developers, while others were subsequently identified by model users. These are broken into four categories: (1) hydrology and soil hydraulics, (2) simulation of pesticide volatilization, (3) method of solution of the transport equation, and (4) deterministic nature of the model. The second version of PRZM, which had been initially released as part of a linked modeling system called RUSTIC (ref.38), has been suitably modified to overcome most of these limitations.

RUSTIC had been designed to link three subordinate models in order to predict pesticide fate and transport through the crop root zone, unsaturated zone, and saturated zone to drinking water wells: PRZM, VADOFT, and SAFTMOD. Due to the incompatibility of SAFTMOD, the model developers decided to drop the SAFTMOD routine from future releases of RUSTIC (personal communication with R.F. Carsel).

The Release 2 version of PRZM incorporates several features in addition to those simulated in the original code (ref.57): specifically, the ability to track metabolites, soil temperature simulation, volatilization and vapor phase transport in soils, irrigation simulation, and a method of characteristics (MOC) algorithm to eliminate numerical dispersion. The fate and transport of the parent compound and up to two daughter species can be simulated simultaneously, or it can track three parent compounds simultaneously. VADOFT (Vadose Zone Flow and Transport Model) is a one-dimensional finite-element that code predicts the flow movement and chemical transport in the unsaturated zone. The user may make use of constitutive relationships between pressure, water content, and hydraulic conductivity to solve the flow equations. VADOFT can also simulate the fate and transport of two parent and two daughter products. In order to perform exposure assessments, the code is equipped with a Monte Carlo pre- and post-processor. The user can vary pesticide and filed input parameters, run the scenario several hundred times, and provide stochastic (probabilistic) outputs of results.

Model Validation

For the model validation efforts, PRZM has been compared with field data in New York and Wisconsin (potatoes), Florida (citrus and tobacco), Georgia (corn), and Hawaii (pineapple), Maryland (tobacco), and North Carolina (tobacco) (ref.56b,59,60,61,62,63), respectively). Most model validation and calibration efforts with PRZM have been successful. Validation of VADOFT has been more limited. See Table 1 near the end of this paper.

Equipment Required
PRZM-2 will run on either an IBM PC 486 or 386 machine or compatible system having 4 megabytes of RAM and at least 4.5 megabytes of free disk space. A special DOS extender called 386 Phar Lap/DOS extender, developed by Phar Lap, Inc., is bound into the application.EXE file of the model. The use of a math coprocessor (8087 family) is required.

Data Required
A computer program, called DBAPE (Data Base Analyzer and Parameter Estimator) (ref.64), was created to encourage and support the use of the PRZM2 model. DBAPE provides an efficient means to obtain soils and meteorologic data needed to run PRZM2 from a data base that contains information on over 8000 agricultural soils and 200 meteorologic stations located throughout the contiguous United States. Soils-related PRZM2 input that can be obtained by using DBAPE includes percent organic matter, wilting point, field capacity, residual water content, saturated hydraulic conductivity and values for the van Genuchten parameters for the soil-water characteristic function. The van Genuchten equation defines the relationship between the volumetric water content and the pressure head, (ref.65) and is related to the solution of the Richards equation of water flow (ref.57). The variability of the important, empirical van Genuchten alpha parameter is high (CV = 20% to 160%, depending on the soil type (ref.57), and therefore is a good parameter to vary in a Mote Carlo Analysis (section 2.6.2).)

Meteorologic data that can be obtained include precipitation, air temperature, pan evaporation, solar radiation, and windspeed. In any case, daily weather records are required. Pesticide retention and degradation properties are also required as a function of depth.

Source
For model acquisition, the person to contact is:

Mr. Bob Carsel
U.S. Environmental Protection Agency
College Station Road
Athens, GA 30612
(TEL) 404-546-3210

3.4.2 Pesticide Leaching Model (PELMO). PELMO is a German adaptation of the original (1984) PRZM model, and it was developed by Klein at the Fraunhofer Institute (ref.66). It is used as a second tier of assessment when the German and northern European leaching criteria are exceeded (section 3.2.1.2).

In case of particularly unfavorable results of the simulation calculations, i.e. strong suspicions with concern for detrimental effects on ground water, registration is refused unless it can be proven unequivocally that under any practical circumstances the substance or its relevant metabolites do not leach to ground water. This next tier of assessment may involve lysimeter studies or monitoring studies.

The Pesticide Leaching Model (PELMO) is a compartmental model simulating chemical movement in the unsaturated soil system within and below the plant root zone. Time varying transport, including advection and dispersion are represented in the program. PELMO is based on the original version of the U.S. PRZM-Model (ref.56a,b) but more processes were included because of limitations in PRZM.

Similar to PRZM, PELMO has two major components: hydrology and chemical transport. While the hydrology component for calculating runoff and erosion is based on the USDA Soil Conservation curve number technique and the modified universal loss equation (same as PRZM), the calculation of evapotranspiration is estimated by using the Haude equation (ref.66) or by direct input of the potential evapotranspiration. Furthermore, PELMO calculates depth dependent temperature in soil by using daily air temperatures.

The calculation of chemical's fate mainly depends on sorption and degradation parameters. Simulation of sorption was improved in comparison with PRZM by including the Freundlich equation (concentration dependency of sorption).

Specific degradation of chemicals is calculated for every soil layer by using biomass (linear relationship to degradation rate), calculated soil temperature (Arrhenius equation), and soil moisture. Usually degradation of first order is assumed, but, if available various orders can be considered. Not all parameters are necessary for doing simulations: dependent on the actual data base simulations can be performed more or less accurately. For screening purpose rough estimations of the chemical's fate can be carried out only by using a K_{oc} value, a half life, and a rate of application.

Thus, PELMO has following additional features in comparison to PRZM:

- calculation of evapotranspiration by using Haude equation or direct input,
- calculation of soil temperatures by using air temperatures,
- calculation of sorption by using Freudlich equation,
- different kinetic orders for biodegradation,
- calculation of biodegradation by using Arrhenius equation,
- correction of biodegradation rate by daily soil moisture content,

Data Required

Climatic Parameters

- daily precipitation
- daily mean temperature
- relative humidity in air at 2.00 pm
- air temperature at 2.00 pm
- potential evapotranspiration (optional)

Soil Parameters (for each soil horizon)

- soil bulk density
- organic carbon content of soil
- ratios for biodegradation (in a lower zone to the upper zone, usually based on the biomass in the soil)
- field capacity (optional)
- wilting capacity (optional)
- particle size distribution (only if field capacity and wilting point are not available)

Pesticide Parameters

- K_{oc}, K_d, or K_f value
- Freundlich exponent 1/n (optional)
- half life
- temperature during degradation study
- factor for rate increase (given a temperature increase of 10°C)
- soil moisture content during degradation study
- exponent describing the moisture dependency (optional)
- kinetics of the degradation study (1st order, 2nd order, ...)
- rate and date of application of the chemical
- application depth

Equipment required

PELMO runs on a PC (MS-DOS) with an arithmetic coprocessor and a EGA- or VGA-graphic card.

Friendliness

PELMO is integrated into an interactive input and output system which allows one to edit and select German climate and soil scenarios as well as chemical properties for simulations. Some climatic and soil scenarios are available. Plotting and printing of important results (e.g. leaching of chemical, concentration in the ground water recharge, concentration in the soil dependent on time and depth) is possible by addition programs.

Source
Fraunhofer Institut
für Umweltchemie und Ökotoxikologie
Postfach 1260
D-5948 Schmallenberg
Germany

3.4.3 Variable Leaching (VARLEACH). The simulation model VARLEACH (Variable Leaching) represents a modified version of the degradation and leaching model CALF (Calculation Flow) which was developed by Walker (ref.67) to predict the persistence and describe the vertical movement of herbicide residues in soil (ref.68a-c). VARLEACH considers the periodic and spatial-vertical variability of degradation rates and sorption of active substances in the soil profile. For this purpose layer boundaries can be defined below which degradation and sorption rates differ from those in the upper layer by distinct factors to be assumed with consideration of the altered abiotic and/or biotic degradation processes and sorption conditions. If no experimental data are available, VARLEACH uses default values reducing the degradation below the selected layer boundary (lower boundary of the cultivated horizon, normally appr. 30 cm) by a factor of 2 and in deeper layers (appr. > 60 cm) by a factor of 4 in relationship to the upper soil layer. The decreased sorption behavior in lower soils is considered by a factor of 0.5 for the zone below the first layer boundary and 0.25 for the lowest layer. Time-variability of herbicides sorption in soil is considered by the following empirical relationship:

$$K_{dt} = K_1 + K_2 * \sqrt{t} \tag{10}$$

where K_{dt} the K_d-value at a time t

K_1 = the K_d-value at the first day, and
K_2 = the slope of the K_d-time dependence.

According to an empirically determined rule (69)

$$K_2 \approx K_1 * 0.1 \tag{11}$$

Time-variability of the degradation of the active substance in soil due to climatic influences can be considered by parameters characterizing moisture and temperature dependence of herbicide degradation in soil.

The vertical water flow and the respective movement of solutes are described by a simple cascade model dividing the soil water into two fractions of different mobility. Only the free, weakly bounded water (between 200 kPa suction and field capacity) and the field capacity exceeding water contents are percolating to lower soil layers.

Data Required
Besides the substance and soil specific degradation data, the application rate, date of application and the water solubility of the active substance are necessary. Actual soil temperature and moisture can be calculated from the weather data of a local service station (ref.69).

Field capacity may be estimated (ref.70)from the granules size distribution and humus content of soil. If there are no data on the water content at 200 kPa available, the water content at 60% of field capacity is used.

Equipment Required
VARLEACH runs on a PC (MS-DOS) with an arithmetic co-processor and can be connected to FREELANCE Graphics. In this case an EGA-or VGA-graphic card is needed.

Friendliness
VARLEACH is integrated in the herbicide advisory system HERBASYS which has been designed to determine selection and application of herbicides, to simulate herbicides leaching, and to predict herbicide degradation and potential ground water hazards (ref.70).

Validity
For the validation of VARLEACH field experiments with three different persistent herbicides (methabenzthiazuron, chlortoburon, metribuzin) were done and showed good conformity of observed and simulated distribution patterns of residues in the soil profile (ref.71)

Source

VARLEACH:
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3.4.4 Erosion-Productivity Impact Calculator (EPIC). Development of EPIC began in the early 1980s as part of a multi-US-agency effort to quantify the costs of soil erosion and the benefits of soil erosion research and control in the USA. EPIC consists of environmental components for simulating erosion, plant growth, and related processes and economic components for assessing the cost of erosion and for determining optimal management strategies (ref.72,73).

EPIC is a simulation model (written in FORTRAN) adapted to mainframe and IBM-PC compatible microcomputers. It uses a daily time step to simulate processes affecting erosion and the effects of erosion on soil productivity. Since erosion can be a slow process, EPIC was designed to simulate hundreds of years if necessary.

The drainage area considered by EPIC is generally small (about 1 ha) and soils and management are assumed to be spatially homogeneous. Vertically, the soil profile can be divided into a maximum of 10 layers. One unique feature of EPIC is the capability to change the depths of soil layers to reflect the effects of erosion.

The components of EPIC include hydrology, weather, erosion, nutrient cycling, plant growth, soil temperature, tillage, and economics. The hydrology model simulates surface runoff volume, peak discharge rate, evapotranspiration, percolation, lateral subsurface flow, drainage, irrigation, and snowmelt. Four options are provided for inputting weather information: (1) daily precipitation, air temperature, and solar radiation can be read into the program; (2) precipitation can be read in and temperature and solar radiation can be simulated; (3) all three variables can be simulated; and (4) relative humidity and/or wind (velocity and direction) may be simulated if the Penman-Monteith equation us used or if wind erosion is considered. All simulations require certain monthly climatic parameters. Wind erosion is predicted using a modification of the Manhattan, Kansas, wind erosion model. Water erosion can be simulated with any of three modifications to the Universal Soil Loss Equation.

The two plant nutrients considered in EPIC are nitrogen and phosphorus. Nitrogen processes simulated include loss of $NO^{-}3$ by runoff and leaching, organic N transport by sediment, denitrification, immobilization, mineralization, and crop uptake. Fertilizer, N fixation, and rainfall can provide N to the system. Phosphorus processes simulated include runoff of soluble P, sediment transport of mineral and organic P, immobilization, mineralization, sorption-desorption, crop uptake, and fertilization.

The EPIC plant growth model simulates all crops with one crop growth model using unique parameter values for each crop. The processes simulated include leaf interception of solar radiation; conversion to biomass; division of biomass into roots, above ground mass, and economic yield; root growth; water use; and nutrient uptake (ref.74).

Soil temperature is a function of the previous day's soil temperature, the present day's air temperature, surface albedo, and solar radiation. The tillage model simulates row height, surface roughness, bulk density changes, and mixing of soil layers, nutrients and plant residue by any tillage operation. The economics component uses a crop budget to calculate crop production costs. Income is determined from simulated annual crop yields.

Since the model's original development in 1985 many improvements have been made. These include: an interactive data entry system; graphical output utilities; extensive soil and weather data bases and crop management data base. In addition, alternative methods to simulate erosion, daily weather, irrigation, fertilization, and tillage have been incorporated. In 1989-1990 a pesticide degradation and movement component was added. This new release is called EPIC-WQ.

Model Validation

Several model validation studies have been reported on the testing of various specific component within EPIC. The N and P models have been tested by comparing simulated results with results measured in a number of field experiments throughout the continental United States (ref.75,76,77,78). The plant growth model has been tested throughout the United States and in several foreign countries (ref.74).

Equipment Required

EPIC will run on an IBM AT PC or compatible system having 640K of RAM and 4 megabytes of disk space. The use of a math coprocessor (8087 family) is not required, but is recommended.

Source

For model acquisition, the person to contact is:

Dr. Jimmy Williams
Agriculture Research Service
U.S. Department of Agriculture
Grassland, Soil and Water Research Laboratory
808 E. Blackland Road
Temple, Texas USA 76502
(TEL) 01-817-770-6508

For the workshop on EPIC training, the person to contact is:

Dr. Verel Benson
Soil Conservation Service
U.S. Department of Agriculture
Grassland, Soil and Water Research Laboratory
808 E. Blackland Road
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(TEL) 01-817-770-6630

3.4.5 Simulator for Water Resources in Rural Basins (SWRRB). The SWRRB model was developed for simulating hydrologic and related processes in rural basins (ref.79). The SWRRB model was developed by modifying the CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) (ref.80) daily rainfall hydrology model for application to large, complex, rural basins. The SWRRB model operates on a daily time step, and daily weather can be input or generated. Because of the provision for subdividing basins and because each subbasin can use a different rain gauge, SWRRB is not limited by drainage area. The basins can be subdivided to account for differences in soils, land use, crops, topography, vegetation, rainfall, temperature, etc. In the vertical direction, the model is capable of working with any variation in soil properties since the soil profile is divided into a maximum of ten layers. A decision support system was developed to assist users in developing input data sets (ref.81).

The three major components of SWRRB are weather, hydrology, and sedimentation. Processes considered include surface runoff, return flow, percolation, evapotranspiration, transmission losses, pond and reservoir storage, sedimentation, and crop growth. A weather generator allows precipitation and temperature to be simulated when measured data in unavailable.

Surface runoff volume is predicted using the SCS curve number as a function of daily soil moisture content. Return flow is calculated as a function of soil water content and return travel time. Return flow travel times can be calculated from soil hydraulic properties or input by the SWRRB users.

The percolation component uses a storage routing model combined with a crack-flow model to predict flow through the root zone. Evapotranspiration is estimated using Ritchie's ET model (ref.82). Transmission losses in the stream channel are calculated as a function of channel dimensions, flow duration, and effective hydraulic conductivity of the channel bed. Pond storage is based on a water balance equation which accounts for inflow, outflow, evaporation, and seepage. The reservoir water balance component is similar to the pond component except it allows flow from principal and emergency spillways. Peak runoff rate predictions are based on a modification of the Rational Formula. Sediment yield is computed for each subbasin with the Modified Universal Soil Loss Equation (MUSLE). The channel and floodplain sediment routing model is composed of two components operating simultaneously (deposition and degradation). Degradation is based on Bagnold's stream power concept, and deposition is based on the fall velocity of the sediment particles. Sediment is also routed through ponds and reservoirs. The crop growth model computes total biomass each day during the growing season as a function of solar radiation and leaf area index (LAI). LAI is computed for each day from maximum LAI and total above ground biomass. The ET component uses LAI to compute plant evaporation. Water and temperature stress factors are used as growth constraints.

Subbasin nutrient yield and nutrient cycling were taken from the EPIC model and modified as necessary for inclusion into the SWRRB model. SWRRB allows for simultaneous computations on each subbasin and routes the water, sediment, and nutrients from the subbasin outlets to the basin outlet.

The pesticide component is taken directly from Holst and Kutney (1989) and is a modification of CREAMS. The processes considered include plant cover and foliar washoff, pesticide decay, pesticide leaching and runoff.

Model Validation

SWRRB has been tested extensively for several widely varying watersheds throughout the U.S. (ref.83), (ref.84). To date these validation efforts have only addressed sediments and water *per se*, and not pesticides and nutrients. However, the pesticide validation efforts for CREAMS are relevant (see above). That information can be found in Knisel (1980) (ref.80).

A new version, called SWRRB-WQ, was released in 1990 (ref.85). SWRRB-WQ is an integrated model that links SWRRB with a water quality model developed by Chapra (ref.86). The integrated model operates on a daily time step and is efficient enough to run for multiple years on a microcomputer. The model tracks the fate of pesticides from their initial application on the land to their final fate in the lake. This allows decision makers to directly predict the influence of upland agricultural management decisions on lake water quality.

Equipment Required

SWRRB-WQ will run on an IBM AT PC or compatible system having 640K RAM and 3 megabytes of disk space. The use of a math coprocessor (8087 family) is not required for short simulations of a limited number of subareas, but is recommended. Long-term simulations or a large number of subareas will require a math coprocessor.

The operation of SWRRBWQ requires that the modeler supply specific watershed and crop information. This information is often not readily available. A PC version of CREAMS and SWRRBWQ was developed by the Computer Science Corporation, Falls Church, Virginia, USA for the U.S. EPA in 1986. It was equipped with a compilation of a variety of existing watershed files. (The importance of runoff modeling is discussed by Urban and Cook (ref.87).) Providing "canned scenarios" enables the user to simulate various agronomic situations at specific regions within the United States.

Source

For model acquisition, the person to contact is:

Dr. Jeff Arnold
Agriculture Research Service
U.S. Department of Agriculture
Grassland, Soil and Water Research Laboratory
808 E. Blackland Road
Temple, Texas 76502, USA
(TEL) 01 817-770-6502

For the workshop on SWRRB training, the person to contact is:

Dr. Verel Benson
Soil Conservation Service
U.S. Department of Agriculture
Grassland, Soil and Water Research Laboratory
808 E. Blackland Road
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(TEL) 01 817-770-6630

3.4.6 CREAMS/GLEAMS. The CREAMS model (ref.80) is a continuous, daily-time-step simulation of edge-of-field losses in runoff water of pesticides, nutrients, and sediment from homogeneous agricultural fields. It has only a rudimentary description of leaching--the model was developed before ground water pollution became an environmental issue. Pesticide degradation is assumed to be exponential. Runoff water is assumed to mix homogeneously with the top 1 cm of soil and pesticide extraction occurs instantaneously and homogeneously depending on K_d (equations), and an empirical "extraction ratio", typically about 0.1, which is the fraction of the pesticide available in the top cm of soil which is extracted. Pesticides which are applied to crop foliage may have different (generally faster) exponential decay rates, and a fraction of the deposit is washed off the foliage after the canopy rainfall holding capacity is exceeded and becomes part of the soil residue available for runoff. Complex slopes and sediment transport processes may be simulated, and sediment enrichment (increase in fines due to preferential deposition of heavier sediment particles during transport) and its effects on pollutant transport capacity are described.

CREAMS has been used world-wide for examining the effects of agricultural management practices such as conservation tillage and agrochemical application methods on surface water pollution potential (ref.88). With its successor GLEAMS it is the most-tested pesticide runoff simulation.

GLEAMS (ref.89), is an extended and completely revised version of CREAMS that has replaced CREAMS for most uses. It includes multiple soil layer input (from 3 to 12 layers of varying thickness) allowing simultaneous calculations of leaching and runoff of agrochemicals. It has detailed pesticide degradation pathway capabilities. The model has been made friendlier: a "front end" data processor allows PC-based interactive input data processing. Unlike CREAMS the hydrology erosion and modules are not run sequentially with pass-through data files, but are linked into a single program. This model is currently one of the most-used for pesticide evaluations worldwide because it provides relatively detailed pesticide processes. It is computationally efficient, and it has received continued strong user support from its developers.

Data Required

Climate:

- daily rainfall
- daily mean, or monthly average max/min temperature
- monthly average solar radiation

Hydrology:

- field geometry and slope(s)
- Soil SCS Curve number
- Soil SCS Hydrologic Group
- Initial soil moisture

Soil texture
Maximum crop rooting depth
on/off moisture levels for irrigation (optional)

For each soil layer:
depth, porosity, % organic matter
field capacity, wilting point

Crop(s):
Winter cover/residue amounts
Leaf area index as f(time)

Erosion:
Surface texture, sediment texture
clay characteristics
slope segment(s) curvature, USLE erodibility
(updatable for multi-year simulations)
Field channel(s) geometry and flow characteristics
(updatable for multi-year simulations)
Impoundment geometry and flow characteristics

For each pesticide and/or metabolite:
no. of metabolites to be considered
initial foliar, soil residues (by layer)
water solubility
soil organic carbon partition constant
foliar washoff fraction, foliar half-life
plant uptake coefficient
soil half-life (by layer)
application rate, date, method of application,
depth of incorporation, foliar fraction
(includes provision for application in irrigation water)

Equipment Required
IBM PC-AT (at least) or compatible with at least 512K of RAM. Math coprocessor recommended.

Support
GLEAMS is actively supported by the developers and is continuously being updated and expanded. The program is available free of charge and includes both PC-executable and FORTRAN source codes.

Friendliness
GLEAMS is a complex model that requires considerable expertise and understanding of the system one is attempting to simulate. The large parameter inputs are helped by interactive parameter-editor programs which edit the input data files and by utility programs for file input and modification and specifying output, which can be large. GLEAMS is shipped with a sample data set for determining that it is running properly.

Validation Level
The CREAMS model has received some 11 years of user evaluation and validation for a wide range of conditions (ref.88). Extensive testing in the US may be summarized by saying that the model is capable of accurate (on the order of 20%) predictions of runoff, sediment, and pesticide losses in surface water, when calibrated for the field in question. Two excellent sources of validation studies are in the CREAMS documentation manual (ref.80) and the study of Lorber and Mulkey (ref.90). Without calibration CREAMs is capable of correctly ranking tillage and other practices which affect erosion and nonpoint pollution.

Simulation of sediment-transported pesticides can be quite good, but real degradation rates and soil sorption coefficients apparently change in time; CREAMS' accuracy in predicting runoff concentrations declines as the time elapsed between application and runoff increases. This will be true of any model that assumes a constant (in time) half life and sorption coefficient (ref.91)

All of the above applies to the surface-water component of GLEAMS, which is simply a friendlier version of CREAMS. GLEAMS' leaching component is much newer, however, and has received less validation. In a recent study by Pennell, et al. (ref.55), GLEAMS was approximately equivalent to PRZM, LEACHMP, MOUSE, and CMLS in the accuracy of its predictions of the depth of greatest concentration of aldicarb and bromide in a Florida field study, though it tended to give less leaching than the others and was not rated highly by those authors. However, none of the models accurately predicted the detailed distribution of aldicarb or bromide with depth. Mueller (ref.92) compared PRZM and GLEAMS predictions with field leaching data for norflurazon, alachlor, and metribuzin. Both models worked well for the first two weeks of the simulation (depth of leaching was well-predicted) but then diverged from field results. Neither model adequately accounted for rapid surface dissipation, probably by volatilization, of the pesticides, and thus overpredicted concentrations throughout the soil profile. Leonard et al. (ref.93) report good agreement between field data and GLEAMS predictions for leaching of the nematicide fenamiphos and two metabolites.

GLEAMS simulates both runoff and leaching simultaneously; this has important applications for comparing tillage and other land management practices for their potential impacts on water quality. A practice which decreases runoff is likely to lead to more leaching, trading one pollution mechanism for another. Conversely, one might look for practices which shunt the water in the direction it will do the least damage.

Several of these studies have been done to validate GLEAMS. (ref.94) compared GLEAMS predictions of water leaching and runoff with 10 years' data from a small watershed in which percolation water was trapped in a subsurface tile drain. In general GLEAMS overestimated runoff and underestimated leaching in the winter, and underestimated runoff and overestimated leaching in the summer. The relative effects of management practices were, however, accurately predicted even without fine-tuning the model to better fit the data. The leaching component was validated using field data from a coastal plain site in Georgia, USA for the nematicide fenamiphos (ref.93). Smith, et al. (ref.95) evaluated the performance of GLEAMS and PRZM using field data from a tracer and two herbicides. The site was a bahia grass test plot in Tifton, Georgia, USA. Both models predicted no runoff, and none was observed. Both models over-predicted the timing and concentration of the tracer peak fairly well. However, the herbicides moved more rapidly and decayed faster than predicted.

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3.4.7 HSPF. The Hydrological Simulation Program-Fortran J (ref.96, 13), is an integrated collection of models which includes the field-scale runoff model ARM (Agricultural Runoff Model) (ref.13,97,98),HSPF also includes programs for modeling runoff from impervious surfaces such as parking lots, modeling water quality resulting from runoff within receiving waters such as rivers; and integration of runoff from fields into watersheds. ARM was originally developed specifically for pesticides but HSPF is now widely used for other chemicals.

HSPF has many unique features. The hydrology is based on the Stanford Watershed Model (ref.99), which is capable of simulating flows within a single storm but requires detailed calibration for the soil at the site--it is essentially an empirical model. Erosion of sand, silt, and clay are simulated along with one organic chemical and its breakdown products. Pesticide soil sorption can be non-instantaneous and a Freundlich isotherm can be specified. One can even specify "hysteresis", i.e., that desorption and adsorption follow different isotherms,

and one can specify bound residues in the soil. Pesticides are assumed to break down exponentially in the soil, but decay constants can be altered during the simulated time. Interflow (the emergence to the surface and contribution to runoff of water--and non-soil-adsorbed solutes--which were part of percolation flow upfield) is modeled in ARM but it is not clear that it does so properly (ref.90).

HSPF has been used worldwide for hydrologic and water quality studies in "upland" watersheds (i.e., one-directional flowing systems--it does not handle estuarine and deep-lake situations where there is reverse flow). It is a very calibration-sensitive model and it has tended to be used in large basin and watershed projects combining point and nonpoint sources and different land use areas. It has been the model of choice for dealing with systems where integration of field data into basins and basin inputs into streams is needed. It has, however, been used only in a small number of studies involving pesticides.

The application of HSPF to a watershed/river system is presented in an "Application Guide" (ref.53), in which the approach to using HSPF is detailed and then exemplified by a study on the Iowa River. A sub-watershed of 52 km^2 was extrapolated to a 7240 km^2 basin. One pesticide (alachlor) was simulated: a comparison of conventional tillage and conservation tillage/contour scenarios indicated that solution-phase alachlor runoff was rather insensitive to erosion control. However, no data were available either for calibration or comparison.

HSPF was used in an innovative calculation of probability statistics for runoff of pesticides, as a function of pesticide soil organic carbon sorption coefficient and half-lives in soil and water (see STREAM description above). Five specific watershed data sets were constructed and runoff was calculated for a range of weather scenarios. This probabilistic analysis makes explicit the stochastic nature of weather effects (ref.52,1).

Data Required

To assemble the data required to run HSPF for a basin or complex watershed/river system is a major project involving months and a multidisciplinary team. ARM, the field-scale runoff subprogram of HSPF, is similar in purpose and complexity to CREAMS and has similar data input requirements (ref.100,98). Differences between CREAMS and ARM are summarized by Lorber and Mulkey (ref.90). ARM is not, however, supported as a stand-alone model but is available only as a fully integrated sub-model of HSPF (Robert Ambrose, personal communication, January, 1992). This means that one must "switch off" the unneeded modules in HSPF, but Donigian (personal communication, January 1992) maintains that this is not difficult.

Equipment Required

IBM-PC-AT or compatible with hard disk and math coprocessor is the minimum system, but will be slow. The program is also maintained in FORTRAN-77 Code for the DEC/VAX and UNIX environments.

Support

HSPF is fully supported by the U.S. Environmental Protection Agency, Center for Exposure Assessment Modeling (CEAM).

Friendliness

HSPF requires considerable expertise and resources to run successfully. Even when a qualified team and data are available for most of the parameters, the program takes weeks to set up and months to run; it is possible to run HSPF for simpler scenarios with less data requirements (ref.13), but smaller-scale models such as SWRRB, AGNPS, GLEAMS and EPIC are probably more appropriate.

Validation level

ARM was shown to simulate toxaphene runoff about as well as CREAMS by Lorber and Mulkey (1982) (ref.90), and a testing/validation project for ARM is described in Donigian, et al. (1977)(ref.98). HSPF has been applied to a wide range of problems successfully (ref.13), but the validation level of ARM for pesticides is probably somewhat less than CREAMS/GLEAMS.

Source (contact)

Robert B. Ambrose, CEAM, U. S. Environmental Protection Agency, Environmental Research Laboratory, College Station Road, Athens, GA 30613-7799, (404) 546-3210

3.4.8 LEACHM/LEACHP. LEACHM, the Leaching Estimation And Chemistry Model) is an umbrella acronym referring to four versions of a model named LEACHN, LEACHP, LEACHC, and LEACHW which are designed for nitrogen, pesticides, soil ions, and water-only, respectively. Referred to by its developers as a "research" model that is usable by others (ref.101,102,19), LEACHM is a leaching and vapor-transport model with no provision for runoff. Hydrologically, it is a numerical solution of both the convective-dispersive solute transport equation and the Richards equation (ref.19), a physical model for transient, unsaturated, vertical water flow as a function of time and depth. Each day is divided into at least ten time segments, but smaller increments are used if needed during water redistribution. The soil is divided into equal depth increments. Water movement may be either downward or upward. Plant leaf and root growth and evapotransporation can occur (described by input parameters).

In LEACHP, many pesticides and different degradation schemes (limited only by user hardware limitations) are possible. The model as received is limited to five pesticides and daughter products but can be modified for more. Pesticide volatilization from the soil surface and interior, and from ponded water is described. Pesticide soil sorption is a linear-isotherm equilibrium, and degradation/transformation kinetics are first-order. Degradation and transformation can be corrected for temperature and moisture fluctuations. Passive uptake of pesticides by plants is allowed. Macropore flow is not simulated, but this, and provisions for a two-site pesticide sorption algorithm are under development.

LEACHP outputs include calculated moisture retention curves for each layer, water content, pesticide and daughter product contents, root density, water uptake, and water and pesticide/daughter product flux between layers and into plant roots for each layer and time specified by the user. It has been successfully used to describe the movement of aldicarb and its sulfone and sulfoxide metabolites (ref.19).

Data required
(the following is taken directly from Hutson and Wagenet, 1989) (ref.102)

Soil properties and initial conditions for each soil segment:
- water content or water potential
- hydrological constants for calculating retentivity and hydraulic conductivity or particle size distribution
- organic carbon content

Soil surface boundary conditions of:
- irrigation and rainfall amounts and rate of application
- mean temperature and diurnal amplitude for each period regarded as having a constant temperature regime (only if a temperature simulation is required),
- pan evaporation (weekly totals).

Crop details (if it is assumed that no crops are present, a control variable allows bypass of the plant-related subroutines):
- time of planting
- root and crop maturity and harvest
- root and cover growth parameters
- a pan factor for adjusting pan evaporation to potential crop evapotranspiration
- lower soil and plant water potentials for water extraction by plants.

Other constants used in determining bottom boundary conditions, time steps, diffusion coefficients and output details. Some of these constants rarely require alteration, but are listed in the data files to define their value for the user and provide the opportunity for change.

Pesticide/breakdown product parameters:
- Saturated vapor density
- Soil organic matter sorption coefficient
- Oxidation/hydrolysis degradation rates in each layer
- Diffusion coefficients
- Application rate, date(s), incorporation depth
- Aqueous solubility

Equipment required
IBM PC-AT or compatible with hard disk. Math coprocessor recommended.

Support
LEACHP is supported by the developers
at Cornell University. Version 2.0 is available on diskette, and instruction is available at Cornell on the use of the model.

Friendliness
LEACHP is a detailed physical model requiring considerable effort and expertise to understand and utilize. Default parameter values are not supplied--the developers believe one must know enough to be able to supply them to be able to use the model appropriately (Hutson and Wagenet, 1989) This is probably the most flexible model available for describing complex pesticide transformations in the soil. Running the model requires the editing of input data files and the compilation of FORTRAN code. Sample data files are distributed with the model. The manual is well written.

Validation Level
LEACHMP was compared with field data by its developers (ref.19,103), and by Pennell, et al. (ref.55) using aldicarb and data from New York and Florida, respectively. It appears that LEACHMP is capable of simulating this case well although the Florida users did not obtain a good simulation of the detailed pesticide distribution with depth. The authors provide a section in the manual for simulating laboratory soil-column data.

Source
Contact R. J. Wagenet or J. L. Hutson, Department of Soil, Crop and Atmospheric Sciences, Cornell University, Ithaca, NY 14853 (607) 255-5459.

3.4.9 RZWQM. RZWQM stands for Root Zone Water Quality Model (ref.104,105,1). Although not currently available, this model is in the testing/evaluation stage by its developers and has been released to a limited number of trial users.

The model was originally conceived as a next-generation one-dimensional leaching model which would have many of the features of LEACHM (e.g., the Richards equation for water redistribution with depth) but be more management-oriented. RZWQM is designed to be applied to agricultural management needs, use modern programming structure and also be able to simulate many of the observed complexities of real field pesticide leaching behavior. For instance, the model is designed to simulate for pesticides, (a) increasing persistence of pesticide residues with time, (b) nonequilibrium sorption, i.e. "kinetic" effects, (c) multiple pesticides, decay pathways and daughter-products schemes, and (d) the behavior of ionized and acid/base pesticides.

The model has grown greatly in complexity since the original concept, because of continued reevaluations of what is both needed and possible, as the computing power available to the average PC user has continued to grow exponentially. RZWQM is now a structured-programming, modular system that includes detailed, interacting modules for:

- Infiltration using the Green-Ampt equation (ref.106)
- Erosion
- Soil inorganic ion chemistry, microbiological processes, and phosphorus, and nitrogen, cycles
- Plant germination and root and top growth, maturity and death; water, nutrient and temperature stress
- Sequential equilibria and kinetics for soil sorption of pesticides including bound residues and hysteresis
- Provision for ionic equilibria of ionic and acidic and basic pesticides
- Macropore flow
- Nonequilibrium extraction of chemicals during runoff
- Management processes including most tillage and irrigation practices.

Data Required
RZWQM has the largest data-input needs of any field-scale model and it is unlikely that it will see general-user status in the near future. It is planned to release the model with five or more "scenarios" representing major crops and US agricultural area. These are complete data sets that will run all modules of the model and allow a user to explore how a particular crop/pesticide/site/climate combination responds to perturbations in the data.

Equipment Required
RZWQM requires at least an 80386 processor with 80387 math coprocessor; a hard disk drive with 6 Mb free; 2Mb of extended memory with 640 Kb conventional memory; DOS version 3.0 or later. An EGA or VGA or better graphics card and monitor, and a laser printer, are not required but are very helpful.

Support
RZWQM is expected to be fully supported by the USDA development team at Ft. Collins, CO. Scenario data set development by cooperators for other situations is expected.

Friendliness
RZWQM has the advantage of having been developed since the introduction of many of the user-friendly utilities and help techniques associated with the current generation of powerful personal computers. An output generator interrogates the user as to the output desired and then assembles the information in two-dimensional and three-dimensional graphs and tables. It is unlikely, however, that any single individual could create a complete RZWQM data set unassisted.

Validation Level
Validation against field data in progress.

Source (contact)
L. R. Ahuja, US Department of Agriculture-Agricultural Research Service, Federal Building, 301 S. Howes St., P. O. Box E, Ft. Collins, CO 80522

3.5 Modeling summaries

3.5.1 Leaching models. Table 1 summarizes the results of six criteria evaluated for ten of the models (ref.107), discussed in this paper. These results were extracted from a report written by the U.S. General Accounting Office that assessed the scientific validity of ground water vulnerability models. In this report, 27 index models and computer simulation models of soil leaching were evaluated. Only those models discussed in this paper are included in this table.

3.5.2 Summary comparison of computer models. Table 2 was prepared as a general overview of the appropriateness of the computer models described in this paper for various tasks.

4. DISCUSSION AND CONCLUSIONS

4.1 Overview
This review demonstrates that a large number of screening models and quantitative models have been developed since the late 1970's to assess pesticide movement in the aqueous phase. Various validation exercises indicate that the quantitative models perform best when the site is relatively small and homogeneous, and when site-specific data are obtained (e.g., soil organic carbon, weather data, degradation rate constants).

There are still many uncertainties in model representations of the environment, as well as in the input parameters. Examples of the former are macropore flow in percolation events and the role of foliar washoff during runoff events. Examples of the latter are uncertainties in degradation rate constants and saturated hydraulic conductivity, as well as uncertainties in runoff curve numbers for vegetation such as turf.

TABLE 1. Selected Summaries of Model Validations from the US - GAO Report (107).

Model	Number of studies[1]	Predictive validity[2]	Inconsistent results[3]	Subcounty analysis[4]	In-dependent replication[5]	Graphical statistical analysis[6]
CMLS	1	1	Yes	No	Yes	Yes
GLEAMS	5	4	Yes	No	Yes	Yes
LEACHM(P)	5	4	Yes	No	Yes	Yes
PESTAN	3	3	Yes	No	Yes	No
PRZM	15	11	Yes	No	Yes	Yes
RZWQM	1	1	N/A	No	No	No
SAFTMOD	1	1	N/A	No	No	No
VADOFT	1	1	N/A	No	No	No
Unnamed #2 (Enfield & Shew, 1975)	1	1	N/A	No	Yes	Yes
Unnamed #13 (Jury et al. 1988)	1	0	N/A	No	No	No

1. Number of studies in which the model was evaluated.
2. Number of studies in which the author concluded that there were at least some positive results.
3. For models for which some positive results have been reported, have negative results been reported either in the same study or across studies? Models that have been tested with only one pesticide in one study or for which no positive results were reported as of 1992 are designated not applicable.
4. Was the model tested at a broader than site-specific scale?
5. Has the model been tested by someone other than its developer?
6. Has the model been evaluated using both graphical analysis and statistical measures of fit

Given the uncertainties in the assessment process, many have tended to focus on reasonable worst case or worst case risk assessments when modeling. For example, it may be appropriate to evaluate the runoff of specific toxic pesticides at sensitive sites using statistically-generated weather data from 1 year, 10 year, or 100 year return storm events.

However, the use of worst case risk assessments when resources are limited can be counter-productive, frequently focusing limited resources on non-problems. Therefore it may be more appropriate to use the stochastic approach, i.e., characterize the key uncertainties in the system and produce hundreds or thousands of runs using the Monte Carlo method. In Monte Carlo analysis, the user selects input parameters to vary as well as their variability. Then the computer randomly selects different combinations of input parameter values to run. This allows consideration of the variability of input parameters (e.g., k, field capacity) that are entered as distributions rather than single values. The program then presents a series of random output values as a cumulative probability distribution function. This is the future that, in some cases, has recently arrived (ref.57,108 a,b). Thus one would be able to characterize a pesticide concentration that would be exceeded 1%, 5%, or 95% of the time. This type of analysis is a tool that could support more detailed and responsible risk assessments.

If a Monte Carlo module is not available for a particular model, users should attempt to estimate the possible range of results anyway. Scientific knowledge should be combined with a common sense approach, as suggested in section 2.6.2.3.

Computer simulation models are increasingly becoming user friendly. Ironically, this could become a drawback to the potential improvements described above. Most computer models should only be used by skilled scientists familiar with the basic environmental processes as well as the model. The risk increases for less competent people to use the models and report the results as the user friendliness of the models increases. One

Table 2. Computer Model Comparisons

Model, source	Type	Hardware Required	Math Type	Time Step/ Weather Data	Degradation [Lumped or Process-Specific]	Processes Simulated				Comments
						Runoff	Erosion	Leaching	Crop Uptake	
GLEAMS, USDA	1°-runoff 2°-leaching	computer	numerical	daily	generally lumped for soil. Hydrolysis may be implicitly included as part of a fractional coefficient.	Y	Y	Y	Y	field scale;handles metabolites and nutrients
PRZM2, US EPA	1°-leaching 2°-runoff	computer	finite difference	daily	lumped in soil but changes with depth allowed	Y	Y	Y	Y	handles metabolites; runoff component field scale; is linked to VADOFT for vadose zone modeling
PATRIOT, US EPA	1°leaching	computer	finite difference	daily	lumped	Y	N	Y	Y	core model is PRZM2; runoff computed for mass balance but not output
PIRANHA, US EPA	1°runoff	computer	finite difference	daily	lumped	Y	N	Y	Y	core models are PRZM2 and EXAMSII; leaching computed for mass balance but not output
Semiempirical, Wauchope & Leonard (1980)	runoff (max. conc. for single event)	calculator	simple algorithm	N/A	lumped	Y	N	N	N	screening level
PESTAN, Method II Enfield, et al. (1982)	leaching	computer	analytical	annual	lumped	N	N	Y	N	easy to use
Method, Enfield, et al. (1982)	leaching	calculator	analytical	annual	lumped	N	N	Y	N	plug flow, no dispersion
HSPF, Johanson, et al. (1982)	runoff	fast computer with large memory, e.g. mainframe	numerical	hourly	user specified	Y	Y	N interflow		comprehensive watershed hydrology and water quality model; sophisticated and expensive to run
SWRRBWQ, USDA	runoff	computer	numerical	daily	lumped	Y	Y	as a loss term only	Y	basin scale; handles nutrients
EPICWQ	1° -runoff 2° -erosion, leaching	computer	numerical	daily	lumped	Y	Y	Y	Y	field scale; pesticide component adapted from GLEAMS
VADOFT, (Huyakorn)	leaching	computer	finite element	daily	lumped	N	N	Y	NA	can be linked to PRZM
LEACHMP, (Wagenet)	leaching	computer				N	N	Y		handles metabolites; transient water flow
PELMO (Klein)	1^o leaching 2^o leaching	computer	finite difference	daily	generally lumped, but special considereation of biodegradation	Y	Y	Y	Y	Several improvements on PRZM1
RZWQM (USDA)	1^o leaching 2^o runoff & erosion	computer	numerical	daily; break-point rainfall	user specified	Y	Y	Y	Y	intend to be used with canned secnarios; ncludes soil chemistry, macropores, microbiology

example of a misapplication is a user who selects a root zone degradation rate constant that is one half of what it should be. This could over predict pesticide concentrations in the root zone by a factor of seven, possibly resulting in unnecessary regulation. This is of special concern in Europe, where the refence standard for drinking water regulation of pesticides in EU countries is O.l μg/L.

An excellent use of models -- computerized or not -- is to rank the contamination potential of various pesticides at a particular crop site, or rank the contamination potential of a given pesticide at various crop sites. Models can also be used to support the need for additional data requirements. Another good use of computer simulation models is to calibrate them for a particular pesticide(s) at an intensively studied site, and then run the model using data from other sites for the same pesticide.

Currently, the least reliable use of models is to evaluate pesticide contamination potential using uncalibrated input parameters with minimal or no field data. A more scientifically valid way of dealing with this type of problem in the near-term future may be to use the probabilistic (stochastic) approach described above.

4.2 Use of runoff and leaching models by environmental regulatory agencies and the pesticide industry
Most pesticide regulatory agencies, the regulated industry, and supporting research institutions recognize that simulation modeling has become a required tool to assess the environmental fate of pesticides. Given the fairly rapid evolution of this field, and the potential for significant error if inappropriate models and/or input parameters are used, several committees have formed to provide some consensus recommendations in this area. Following is a brief summary of some of these efforts.

4.2.1 The European Crop Protection Association (ECPA). The ECPA Water Task Force recently published "The Regulatory Use of Lysimeter Studies and Computer Modeling for the Evaluation of Pesticide Mobility in Soil (Technical Monograph No. 16, March 1993, Bruxelles). Brief summaries of the following models were provided based on the authors' experiences: PRZM, PRZM2, PELMO, PRZM-FhG, LEACMP, SESOIL-FhG, PESTLA, CALF, and GLEAMS. Their recommended progression of leaching modeling, in a tier scheme, was as follows. The modeling studies are intended to be done in parallel to field studies.

screening assessments --> predictive modeling --> calibrated modeling (calibrated with field data) --> detailed modeling.

4.2.2 The German tiered approach to complying with EEC Directive 91/414. Computer simulation modeling plays a key role in Germany's approach to pesticide assessment (ref 41). A PELMO prediction exceeding 0.1 μg/L below 1 meter triggers the requirements for a lysimeter study. A prediction exceeding 10 μg/L indicates the product may not be registerable.

4.2.3 Generic requirements in the European Community (EC). In January, 1995, the EC published Document 1654/IV/94. Appendix 4 of Annex III A requires potential pesticide registrants to predict environmental concentrations of pesticides in ground water, soil, and surface water - PEC_{GW}, PEC_s, and PEC_{sw},respectively. The use of simulation models is allowed, and even encouraged, but minimal technical guidance is provided. As of 1995, runoff modeling has not been required but the use of PELMO to predict worst case leaching scenarios has been encouraged.

4.2.4 Pesticide modeling in the U.S. EPA. The U.S. EPA currently uses a tiered system for runoff and EEC calculations in support of ecological risk assessment. For ground water assessments, modeling is done both at the screening level and also to evaluate results of field studies and possible mitigation measures.

The surface water EEC tier system has three tiers, of which two are currently completed. The first tier uses screening models to remove from consideration pesticides likely to pose little ecological risk. Currently a crude, "back of the envelope" method keyed to solubility and application method is used to estimate exposure at the screening level. At the second tier, a single site is chosen and the simulation is run at the site for 30+ years. The site is chosen to represent sites that are actually used for the crop in question but are more prone to runoff than most of the sites used for that crop. Generally, PRZM and PRZM2 are used for the calculations but GLEAMS

is also used in some situations. The loading information is transferred to EXAMS which calculates the EEC's if an EEC calculation is needed. The output is summarized and ranked and used to generate cumulative probability distributions of runoff events or EEC's. The value with a 1 in 10 year return frequency is used for comparison to the toxicological end points and to generate the ecological risk assessment. The third tier surface water assessment is still in development, but will use multiple sites simulated from multiple years. This will generate an overall estimate of exposure over the whole range of use sites in question. This level analysis also can be used to determine which sites are of concern and suggest geographically based mitigation strategies.

Ground water assessments can include results of the screening models CHEMRANK, CMLS, and PATRIOT, and the more data intensive models, PRZM and PRZM2, however, in contrast to surface water assessments, models are used in a comparative mode only. Results are used to set priorities for further assessment, either by identifying specific pesticide alternatives on which to focus evaluation, or to determine if monitoring is needed. Data collected in field-scale ground water monitoring studies conducted by registrants to support registrations are used to calibrate models (PRZM, PRZM2, LEACHM), and subsequently to simulate pesticide behavior over longer time periods. Another fundamental use of models is to compare the relative effect of alternate mitigation measures aimed at preventing ground water contamination. Follow-up regulatory action is based on modeling and monitoring results, if a comparison of the results with human or ecological toxicological end points indicates a level-of-concern has been or is likely to be exceeded.

5. RECOMMENDATIONS

Leaching: screening-level assessments

1. There are several, easy-to-use, index/leaching criteria available to indicate whether concerns should be raised for ground water contamination potential about a particular pesticide or to rank pesticides relative to each other. The Attenuation Factor computation (ref.43), the GUS index calculation (ref.42), and the mobility and persistence leaching criteria (ref.30) are used most frequently and appear to be most reliable at the screening level. The model by Jury et al. (ref.5) also appears to be appropriate for these applications. These models should be applied at an early phase of ground water contamination assessments. For important applications, it may be appropriate to apply two screening models based on different principles, e.g., the leaching criteria and the Attenuation Factor, static and dynamic approaches, respectively.

Runoff: screening-level assessments

2. Screening models for assessing runoff potential do not yet have the same wide acceptance. As of 1992, it would probably be best to screen pesticides for runoff potential using the STREAM approach (ref.52)(a series of precomputed runoff nomograms) or the SCS Goss index (ref.47). Unfortunately, all of the crop scenarios used in STREAM were from U.S. sites and may have limited applications elsewhere.

Leaching: computer simulation modeling

3. When quantitation of pesticide leaching potential is required, PRZM2 (or a modified version such as PELMO (Germany)) would be appropriate for most situations. Like other models it has certain limitations. But it has been validated in several different pesticide/site scenarios, it has reasonable documentation, and is used widely in the U.S. and Europe. Other models such as GLEAMS, LEACHM, and CALF also seem to be scientifically acceptable, but these have more limited distribution and support.

Runoff: computer simulation modeling

4. When quantitation of pesticide runoff potential is required, the GLEAMS model is appropriate for most scenarios involving simple, field-scale drainage patterns. The more complex and difficult to use SWRRBWQ model is more appropriate when complex drainage patterns such as watersheds are being modeled and/or when site-specific features such as drainage channels, detention basins, or gulches need to be modeled. HSPF is appropriate when very intensive runoff modeling can be supported and hourly output is required.

Proper use of computer modeling

5. The most appropriate use of these computer simulation models is to rank the contamination potential of a particular pesticide at several sites, or rank several pesticides at one site. Another excellent application

of these models is to calibrate them to fit the results of an intensive field study at one site, and predict what might happen following application of the pesticide to another site. The least valid application is predicting offsite impacts using inappropriate or uncalibrated input parameters. However, this approach can be made much more credible by conducting an uncertainty analysis such as with the Monte Carlo method. Such an approach would describe the variability in results that one might expect for a particular site/pesticide scenario.

Recommendation for future work

6. These models have been applied rarely, if at all, to agricultural scenarios in tropical climates. (Work has been done in this area in Hawaii for tropical crops but in a subtropical environment.) Validation studies are needed in these types of environments. In order to facilitate such studies, it would be helpful for government organizations to compile several decades of daily weather data for various sites in their respective countries. In many cases, basic data on pesticide and water retention properties in tropical soils should also be generated, e.g., organic carbon, field capacity, and wilting point by horizon.

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Glossary of Terms

Algorithm -	the numerical technique embodied in the computer code (ASTM, 1984)
Calibration -	a test of a model with known input and output information that is used to adjust or estimate factors for which data are not available (ASTM, 1984).
Compartmentalization-	division of the environment into discrete locations in time or space (ASTM, 1984).
Computer Code-	(computer program) the assembly of numerical techniques, bookkeeping, and control language that represents the model from acceptance of input data and instructions to delivery of output (ASTM, 1984).
Conceptual Model -	qualitative depiction of a specific environment that describes the linkages between the different compartments. A conceptual model is required before a quantitative simulation model can be developed.
Mathematical Model -	an assembly of concepts in the form of a mathematical equation that portrays understanding of a natural phenomenon (ASTM, 1984)
Sensitivity -	the degree to which the model result is affected by changes in a selected input parameter (ASTM, 1984)
Validation -	comparison of model results with numerical data independently derived from experiments or observations of the environment (ASTM, 1984).
Verification -	examination of the numerical technique in the computer code to ascertain that it truly represents the conceptual model and that there are no inherent numerical problems with obtaining a solution (ASTM, 1984).